Effects of addition of engineered ZnO nanoparticles on the stability of colloidal suspensions containing TiO$_2$ interacting with sandy soil

Abstract

The stability of colloidal suspensions of engineered nanoparticles in the environment is of great interest for the risk assessment and treatment of hazardous materials. The relevance of this study is due to the evidence that engineered nanoparticles have been produced and used in commercial products in large scale, especially ZnO and TiO$_2$, which are transported through the environmental components interacting with soil and water, representing the high potential impact on the ecosystems. In this research, we newly investigated the influence of nanoparticles of zinc oxide (NPZnO) on the behavior of nanoparticles of titania (NPTiO$_2$). The impact of parameters such as pH, zeta potential, ionic strength, electric conductivity, suspended nanoparticles size of the colloidal suspensions containing hazardous nanoparticles on its stability, were studied using experimental and theoretical approaches. Leaching experiments were carried out within a sandy soil column model. It was found that the NPTiO$_2$ in suspensions enhance the stability of the nanoparticles colloidal suspensions, keeping higher nanoparticles concentrations, while NPZnO promotes rapid aggregation, improving the soil particle collector efficiency with a lower concentration in equilibrium in the colloidal suspension, which can be used for promoting environmental impact attenuation and mitigation.

Keywords: Stability, nanoparticles, colloidal suspensions, attachment, collector efficiency.

1. Introduction

The metal oxide engineered nanoparticles are used in a wide range of commercial products, leading to an increasing interest in the behavior of these materials in the environment. Nanoparticle deposition and mobility in porous media is strongly dependent on not only pore size and collector surface energy with their organization, but on the physicochemical properties of the colloidal suspensions (ionic strength, pH, presence of natural organic matter), nanoparticle surface properties and functionalization, and flow rate and the soil particles surface properties. These parameters that affect the interactions between the nanoparticles and the solid media, also control nanoparticle aggregation, which may subsequently influence the balance between free migration of the nanoparticles and deposition (Espinasse et al., 2007; Domingos et al., 2009; Fang et al., 2009; Oliveira et al., 2014; Oliveira et al., 2016). Nanomaterials can be emitted into the environment throughout their "life cycle" which is understood as the production, use, and disposal of nanomaterial that is discarded in the environment (Son et al., 2015), as shown in Figure 1. It shows the multiple and complex processes and phenomena of the production, discharge into the environment, and interactions with the components schematically. The studies on these emissions and discards are carried out for a comprehensive evaluation regarding their potential toxicity, environmental risk when interacting with ecosystems and living species, and consequently are considered as emerging pollutants with restricted knowledge of their real impact on the actual society (Chai et al., 2015).

Studies for hazardous assessment of ENPs on different food-chain level organisms, such as bacteria, algae, fish, crustaceous and nematodes, indicated that metallic ENPs (TiO$_2$, Ag, ZnO and CuO) are toxic at environmentally relevant concentrations (Tourinho et al., 2012; Holden et al., 2014). These studies have consistently shown that colloids, as well as organic and inorganic matter are essential factors that affect the mobility of metallic ions in landfill leachates, with less than 10% of total concentrations of metal as free ion. The introduction of the engineered nanoparticles of TiO$_2$ (ENPTiO$_2$) in the environment is due to processes such as mining, TiO$_2$-enabled product fabrication, product use, product recycling and disposal to the aquatic environment through the disposal of the industrialized product in landfill systems.

Elizabeth Mendes de Oliveira$^{1,3}$
https://orcid.org/0000-0002-9205-8570
Jonni Guiller Ferreira Madeira$^{1,4}$
https://orcid.org/0000-0001-5676-1720
Cintia de Faria Ferreira Carraro$^{1,5}$
https://orcid.org/0000-0002-1476-7005
Mara Carolina do Carmo Paresque$^{2,6}$
https://orcid.org/0000-0002-0530-4172
Jose Adilson de Castro$^{2,7}$
https://orcid.org/0000-0001-8054-9236

$^1$Centro Federal de Educação Tecnológica - CEFET/RJ, Departamento de Disciplinas Básicas e Gerais, Angra dos Reis – Rio de Janeiro - Brasil.
$^2$Universidade Federal Fluminense – UFF, Departamento de Engenharia Metalúrgica, Volta Redonda – Rio de Janeiro - Brasil.

E-mails: $^3$beth.mendes.oliveira@gmail.com, $^4$gaiada123@hotmail.com, $^5$cintia.carraro@cefet-nj.br, $^6$paresquemara@gmail.com, $^7$joseadilsoncastro@id.uff.br
Another critical and abundant nanoparticle emission from industrial processes, which is commonly present in our lives, is the zinc oxide nanoparticles (NPZnO) that are widely used in modern goods. NPZnO is among the most frequently used nanoparticles having different uses such as environmental remediation and sunscreen application. Due to their increased usage and disposal, NPZnO is likely to enter the environment in large quantity, with natural soil particles being the collector, representing a potential risk to soil organisms (Bergstrom, 1997; Jaisi et al., 2014; Cupi et al., 2015, Baragana et al. 2020, Shrivastana et al. 2019).

Thus, this study aims to investigate the effect of the addition of NPZnO into the interaction and mobility of NPTiO$_2$ in water colloidal suspensions within a natural sandy soil component. This soil was chosen due to its characteristics of a typical sandy soil and represents a model study to analyze the impact of the residue’s disposal containing these materials in soil components. The analysis was carried out using theoretical and experimental approaches in a complementary manner to determine the model parameters and soil particles collector efficiencies, which enables the prediction of long-term attenuation of the contaminants in the soil compartment.

2. Materials and methods

2.1 Theoretical model

In porous media, the transport of nanoparticles can be described by phenomena that intercepts the nanoparticles by the media, agglomeration, and sedimentation. This occurs due to gravity and effective diffusion into the colloidal suspension because of the Brownian motion, being captured by the particles of media that behaves as the collector. Notably, in the case of nanoparticles, the gravitational effect is negligible. However, we can include a term for the first-order colloidal deposition (Fang et al., 2009; Castro et al., 2011; Yang et al., 2018, Oliveira et al. 2019) and the resulting governing is Eq. 1. Where $t$ is the time, $v$ is the fluid velocity vector, $k$ is the deposition rate coefficient, $C$ is the nanoparticle concentration and $D$ is the effective diffusion coefficient of the nanoparticles within the interstitial of the soil particles wetted with the colloidal suspension.

\[
\frac{\partial C}{\partial t} + v \cdot \nabla C = D \nabla^2 C - kC \tag{1}
\]

In order to determine the deposition rate coefficient, $k$ the rupture curves are integrated using Eq. 2, where $t_p$ is the average travel time of the particles through the channel, $q$ is the flux, $N_0$ is the total amount of nanoparticles fed, and $t_f$ is the total time of the feeding pulse through the column. Eq. 3 can express the maximum travel distance, defined by the distance at which 99.9% of the nanoparticles have been removed from the solution. Herein, $C_f/C_0 = 0.001$, $L_{max}$ is the maximum column length, $L$ is the column length, $C_0$ is the initial effluent nanoparticle concentration, and $C_f$ is the final effluent nanoparticle concentration after the breakthrough curve has reached a plateau and $\alpha$ is the attachment efficiency for nanoparticle deposition (Kretzschmar et al., 1997, Tufenkji et al., 2004). Also, $d_c$ is the diameter of the soil particle spherical collector, $f$ is the porosity of the porous medium, and $n_0$ is the single-collector contact efficiency.

\[
\kappa = -\frac{1}{t_p} \ln\left(\frac{q}{N_0} \int_0^{t_f} C(t)dt\right) \tag{2}
\]
The overall single-collector contact efficiency for deposition in saturated porous media can now be written as the sum of the individual contributions for each transport mechanism resulting in Eq. 5.

\[ \eta_0 = 2.4A_s^{1.13}N_{R}^{-0.081}N_{Re}^{-0.715}N_{d}^{0.052} + 0.55A_s N_{R}^{1.675}N_{A}^{0.125} + 0.22N_{R}^{0.24}N_{G}^{1.11}N_{vdW}^{0.053} \]  

The dimensionless parameters are as follows:

- \( A_s \): porosity-dependent parameter of Happel's model
- \( A_s = 2(1-(1-f)^{1/3})/(2-3(1-f)^{1/3}+3(1-f)^{1/3}) \)
- \( N_{R} \): aspect ratio; \( N_{R} = d_p / d_c \)
- \( N_{Re} \): Peclet number; \( N_{Re} = U_d / D_{\infty} \)
- \( N_{vdW} \): van der Waals number; \( N_{vdW} = A / kT \)
- \( N_{A} \): attraction number; \( N_{A} = N_{vdW}N_{vdW}^{1/3}N_{vdW}^{-1/3} \)
- \( N_{G} \): gravity number obtained by combining three dimensionless parameters; \( N_{G} = 2A_s^{1/3}N_{A}^{1/3}N_{Re}^{-1/3} \)
- \( f \): porosity of a porous medium
- \( a \): radius of spherical collector
- \( a_p \): radius of nanoparticle
- \( d_c \): diameter of spherical collector; \( d_c = 2a_c \)
- \( d_p \): diameter of nanoparticle; \( d_p = 2a_p \)
- \( d_p \): diameter of nanoparticle; \( d_p = 2a_p \)

2.2 Soil characterization
The soil samples were collected and the parameters measured for the characterization of the soil indicating the physical and chemical characteristics as presented in Table 1. The soil characterization was carried out in a previous study and reproduced for the present analysis (Oliveira et al. 2014, 2017, 2019).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of soil and aspect</td>
<td>(-)</td>
<td>Sandy/Granulated solid</td>
</tr>
<tr>
<td>Density of soil</td>
<td>(g.cm(^{-3}))</td>
<td>2.63</td>
</tr>
<tr>
<td>Liquidity limit</td>
<td>(%)</td>
<td>54.83</td>
</tr>
<tr>
<td>Plasticity limit</td>
<td>(%)</td>
<td>32.79</td>
</tr>
<tr>
<td>Plasticity index</td>
<td>(%)</td>
<td>1.66</td>
</tr>
<tr>
<td>Optimal humidity</td>
<td>(%)</td>
<td>20.93</td>
</tr>
<tr>
<td>Diameter of soil particle:</td>
<td>(µm)</td>
<td>2-3</td>
</tr>
<tr>
<td>pH</td>
<td>(-)</td>
<td>8.92</td>
</tr>
<tr>
<td>Cation exchange capacity (CEC)</td>
<td>(cmol.kg(^{-1}))</td>
<td>7.35</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>(mV)</td>
<td>-17.45</td>
</tr>
<tr>
<td>Percentage of organic matter</td>
<td>(%)</td>
<td>2.3</td>
</tr>
<tr>
<td>Humidity at 105 °C</td>
<td>(%)</td>
<td>9.62</td>
</tr>
<tr>
<td>Total titanium</td>
<td>(mg.kg(^{-1}))</td>
<td>1221.02</td>
</tr>
<tr>
<td>Total zinc</td>
<td>(mg.kg(^{-1}))</td>
<td>55.73</td>
</tr>
</tbody>
</table>

2.3 Experiment
The column experiment setup was prepared in PVC tubes of 20 cm high and 5 cm in diameter (Tassi et al., 2011, Oliveira et al., 2017, Yang et al., 2018). The lower portion of the tube was equipped with a paper disc (filter) and supported
in a fine mesh (to prevent the passage of soil particles) and connected to a reducer to facilitate the collection of the leaching liquid outlet. The soil columns were packed manually with uniform layers with 10 cm of air-dried sandy soil, commonly used as landfill layers. The columns were initially saturated with deionized distilled water (DDW) by a capillarity process. Figure 2 illustrates a schematic view of the column experiment setup. The suspensions of NPTiO\(_2\) were prepared following the procedure previously reported by the authors (Oliveira et al., 2016; Oliveira et al., 2017). The colloidal suspensions were produced by vigorous mixing of the nanoparticles of TiO\(_2\) and ZnO in three combinatory mixing procedures of nanoparticles, 250 mL and milli-Q water. The nanoparticles were purchased from Sigma-Aldrich and the stable colloidal suspensions prepared using vigorous agitation (24 h at 600 rpm) and 10 days of the decantation and collected the supernatant suspensions. The NpTiO\(_2\) and NpZnO are specified with 99.9% of phase purity composed of anatase and zincite 99% purity, respectively. TiO\(_2\) nanoparticles presented average specific surface area of 32 m\(^2\)/g and average particle size of 35 nm. The zincite presented surface area of 30 m\(^2\)/g and average size 30nm. An aqueous TiO\(_2\) and ZnO nanoparticle suspensions were prepared by vigorously rotating during 24 h on a rotary suspension mixer, and then transferred into beakers which were allowed to settle undisturbed for 10 days. The supernatant from the beakers which contained unsettled ZnO and TiO\(_2\) nanoparticle suspensions (ZnO and TiO\(_2\) nanoparticles colloids) were collected after 10 days and used for the leaching experiments. The protocol of these preparations has been applied for a wider number of nanoparticles colloids preparations and analysed using different techniques (Oliveira et al., 2014, 2017, 2019, Fang et al., 2009).

The Ionic strength (I) of the colloidal suspensions at inlet and outlet flows of the column were calculated using the equation relating the measured electrical conductivity (EC) and ionic strength (I), as shown in Eq. (6). The nanoparticles characteristics and parameters specifications of the colloidal suspensions are listed in Table 2.

\[ I = 0.0127 \times EC \]  (6)

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

Table 2 - Specifications of the nanoparticles and characteristics of the colloidal suspensions.

<table>
<thead>
<tr>
<th></th>
<th>Suspensions TiO(_2)</th>
<th>Suspensions ZnO</th>
<th>Suspensions ZnO + TiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase purity</td>
<td>99%</td>
<td>99%</td>
<td>---</td>
</tr>
<tr>
<td>Surface area</td>
<td>30 m(^2)/g</td>
<td>≥ 15 m(^2)/g</td>
<td>---</td>
</tr>
<tr>
<td>Average size: (d_p)</td>
<td>35 nm</td>
<td>30 nm</td>
<td>--</td>
</tr>
<tr>
<td>Initial Concentration</td>
<td>2 g. L(^{-1})</td>
<td>1 g. L(^{-1})</td>
<td>(ZnO (1 g) + TiO(_2) (1 g)). L(^{-1})</td>
</tr>
<tr>
<td>Stabilized Concentration</td>
<td>32.5 mg. L(^{-1})</td>
<td>1.7 mg. L(^{-1})</td>
<td>ZnO (5.6 mg. L(^{-1}))</td>
</tr>
<tr>
<td>TiO(_2) (2.2 mg. L(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluid absolute Temperature: (T)</td>
<td></td>
<td>301K</td>
<td></td>
</tr>
<tr>
<td>Nanoparticle density: (\rho_p)</td>
<td>4.1 g.cm(^{-3})</td>
<td>5.61 g.cm(^{-3})</td>
<td>ZnO (4.027 g.cm(^{-3}))</td>
</tr>
<tr>
<td>Density of fluid: (\rho_f)</td>
<td>1 g.cm(^{-3})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hamaker constant: (A)</td>
<td>(3 \times 10^{-21} - 4 \times 10^{-20}) J</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Subsequently, the concentrations of the nanoparticles and distribution of the size of their aggregates and the stability of the solutions and the ionic activities were measured respectively by ICP-OES, Nanosight LM10 and ZetaSizer nano techniques. ICP-OES was used to analyze the dilute colloid elemental analysis and attributed to the nanoparticles, the Nanosight technique was used to obtain the particle size distributions and concentrations at the inlet and outlet of the column.

3. Results and discussions

The results and discussions addressed in this section aim to evaluate the effects of the addition of NPZnO to stabilize the colloidal suspensions containing NPTiO₂ and the corresponding effects of the interactions during percolation with sandy soil collector using controlled soil column experiments and theoretical analysis. For this purpose, three columns were constructed: NPTiO₂, NPZnO, and (NPTiO₂+NPZnO) to evaluate the effects of NPZnO on the stability of the suspensions under study. In Figure 3, the measured values of the size distributions and correspondent concentrations in the suspensions are shown. Nanosight Tracking Analysis (NTA) technique analysis was used to determine the values before and after the colloidal suspensions passing through the soil column experimental setup, as shown in Figure 2. Three leaching colloidal suspensions were analyzed. Figure 3 presents the measured values for the size distributions at the inlet and outlet flows passing the column filled with sandy soil. The prepared colloidal suspensions were fed with the suspensions of TiO₂, ZnO, (TiO₂ and ZnO), respectively, under the same flow rate. As can be observed in the three cases, the results revealed that agglomeration occurs when the colloidal suspension passes through the soil column, evidenced by the increase of the size and decrease of the concentration of nanoparticles at the outlet flows of the suspensions.

However, the concentration decreases sharply as NPZnO is added into the NPTiO₂ colloidal suspension. These results confirm that the soil particles captured the nanoparticles of the suspensions and worked as an effective collector barrier for the plume contamination. The higher stability of the suspensions containing hazardous nanoparticles mixture with NPTiO₂ is confirmed by the measurements of nanoparticle tracking analysis (NTA), which allows the evaluation of clustering formation and monitoring of the average size of the nanoparticles, as shown in Figure 4. A comparative plot of the size distributions of the nanoparticles in the colloidal suspensions collected at the outlet flow of the soil column is shown in Figure 4. Therefore, the effects of the NPZnO on the effectiveness of the soil column can be estimated by the number of nanoparticles removed from the suspensions. The impact of the presence of the NPTiO₂ plays a significant role in decreasing the effectiveness of the retention. Meanwhile, the NPZnO sharply increases its efficiency. Therefore, we can recommend the addition of controlled quantities of NPZnO to reduce and avoid effluent contamination by NPTiO₂. In Table 3, shown are the parameters of the colloidal suspensions measured at the outlet flow of the columns. The measured zeta potential, pH and nanoparticles agglomerated average sizes are compatible with those obtained for the electric conductivities and correspondent calculated ionic strength, using Eq. 6. The correlation of the effect of the ionic strength on the rates of deposition and complexation of the nanoparticles is in qualitative agreement with a similar previous study (Fang et al., 2009).
The soil capability to retain the nanoparticles is comparatively presented in Figure 5(a) using the calculated parameter representing the attachment efficiency of the soil under the flowing conditions of the experiments. Figure 5(a) shows the attachment efficiency of the soil column during the suspension’s percolation and interactions of the nanoparticles with the soil particles. As can be observed, the suspensions with NPZnO presented higher efficiency attachment when compared with the NPTiO₂. The addition of NPZnO into the NPTiO₂ suspensions increased attachment efficiency and improved the ability of the soil particles to retain the hazardous nanoparticles. Thus, the addition of NPZnO into the leaching fluid is expected to enhance the efficiency of the soil collector of the landfills and protect the environment on the landfill site, avoiding further impacts on the ecosystems. It is worthy to note that the general behavior of the colloidal suspension with NPZnO within the covering layers is achieved by combining the interactions into the suspension and attachment in the soil structure. Figure 5(b) shows a comparison of the predicted and measured outlet concentrations for the experimental runs and a reference study for a similar soil collector. Good agreements of the predicted and measured values are achieved.
The strength of these effects depends on the amount of the addition of ZnO and the dissolved organic matter (DOM) on the colloidal suspension. The stability of metal oxide nanoparticles in aqueous solutions depends mostly on the ionic strength and pH. Figure 6 (a) describes the influence of pH on suspension stabilization. In the three cases mentioned above, the NPTiO₂ suspension is characterized by its high stability. However, as NPZnO is inserted into the suspensions, it promotes an increase in pH and, consequently, a reduction of the ionic strength, resulting in higher adsorption of nanoparticles in the soil. At the most elevated pH investigated above the pH_{pzc}, it is observed the most negative zeta potential. These data indicate that as the pH suspensions approach, the pH_{pzc} aggregates are rapidly formed due to the ionic strengths of the soil.

According to Figure 6 (b), the colloidal suspensions of ZnO nanoparticles showed to be more stable at lower ionic strength, as expected. These data showed that the zeta potential increased with the increase of ionic strength, which means that the NPZnO interaction is highly repulsive at low ionic strength. Under these conditions, NPZnO begins to undergo sedimentation. High ionic strength results in the compression of the EDL (electrical double layer) and consequently decreases the EDL repulsive forces such that the net repulsive energy barrier between ZnO nanoparticles decreases. The most significant distance L_{max} was obtained for the NPTiO₂ suspension, which is consistent with the lowest deposition observed for the NPZnO colloidal suspension. The L_{max} indices decreased in the following order of the suspensions: NPTiO₂ > NPZnO > (NPTiO₂+NPZnO). The results suggest that NPTiO₂ suspensions travel more considerable distances from their high stability region, as indicated by the zeta potential, resulting in a longer interaction time between the different nanomaterials present in the soil and the leaching suspensions.

![Figure 6](image-url)  
Figure 6 - The plot of the effects of the pH (a) and Ionic Strength (b) on the zeta potentials of the colloidal suspensions measured in this study.

4. Conclusions

The colloidal suspensions with the addition of nanoparticles of zinc oxide percolating within a model sandy soil column were addressed. The experimental results revealed that the stability of NPTiO₂ colloidal suspensions is strongly influenced by NPZnO. Our research clarified and emphasized the selected important set of parameters (pH, ionic strength, zeta potential, pH_{pzc}, average soil particle size, dissolved organic matter, soil characteristics, pore structure, and surface charges) that had the main impacts on the quantification of stabilization features of the colloidal suspensions and soil collector efficiency. The zeta potential is an essential indicator for measuring the stability of the colloidal suspensions containing nanoparticles. This parameter was used to quantify the characteristics of the outlet flow of the suspensions. The nanoparticles sizes and their distribution together with the concentration of zinc oxide and titania (NPTiO₂) on the flowing suspensions were quantified to indicate the potential of harmfulness to the environment. Using the results of the leaching column experiments, we demonstrated that about two units of pore volume are enough for the soil column to retain the harmful nanoparticles when sandy soil is used. With basis on the results, we can predict the adequate design of the soil layer with higher efficiency collector features to minimize the impact of the disposal of hazardous nanoparticles discharge in the landfills and carried to the environment components. The accurate prediction of the soil collector efficiency allows the secure estimation of the contention layer thickness into the landfills, which maximizes the capture of hazardous suspended nanoparticles carried by the colloidal suspensions, in a long-term perspective of attenuation and mitigation.

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