Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1163513

57 (2016) 26196–26203
November

Experimental investigation of stability and transport of TiO_2 nanoparticles in real soil columns

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Received 22 November 2015; Accepted 4 March 2016

ABSTRACT

This study aims to explore the stability of TiO_2 nanoparticles in soil suspensions and their transport behavior through real soil columns. A classical filtration theory was used to describe transport behaviors of TiO_2 nanoparticles. The results illustrated that TiO_2 nanoparticles could remain suspended in soil suspensions even after settling for 8 d. At comparatively higher dissolved organic matter (DOM) and low ionic strength (IS) containing soils, considerable portion of TiO_2 nanoparticles (32–34%) suspensions was observed in sedimentation experiments after 24 h. In addition, zeta potential (ZP) of soil suspensions as a function of soil pH, suggested that ZP played significant role than soil pH. In soils containing comparatively higher DOM, a considerable portion of TiO_2 nanoparticles (51.8–90.6%) readily passed through soils columns, while TiO_2 nanoparticles were retained by soils with comparatively higher ISs. The estimated travel distances of TiO_2 nanoparticles in soils ranged from 45.03 to 625.86 cm, representing potential environmental risk of TiO_2 nanoparticles to the environment.

Keywords: Sedimentation; Ionic strength; Dissolved organic matter; Classical filtration theory

1. Introduction

The rapid development in nanotechnology and the production, consumption, and disposal of nanomaterials, they will inevitably and ultimately enter the environment. TiO_2 nanoparticles (TNPs) are one group of the most extensively utilized nanomaterials in cosmetics, sunscreens, paints, coatings, and increasingly for the photo catalytic degradation of various pollutants in water, air, and soil matrices [1–6]. TNPs become challenging and are viewed as an emerging pollutant due to their neurotoxicity to animals, capability of causing oxidative stress in human cells [7,8] and genetic instability in mice [9]. After liberating into the environment, TNPs have the capacity to be transported in the subsurface. Consequently, nanoparticles may get into groundwater [10] and enter into the food web through bioaccumulation [11]. Therefore, it is important to understand the transport of TNPs in natural porous media.

Stability of nanoparticles in aqueous solution is a key factor controlling their transport and ultimate fate in aqueous environments. The stabilization of nanoparticles in aqueous solution needs to be fully addressed before research in transport. However, a limited number studies have been published on the stability of a variety of nanoparticles in aqueous solution under various simulated environmental circumstances or to form

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submicron aggregates, and consequently their mobility [12–15]. The aggregation of TNPs and the electrostatic interaction between TNPs and the surfaces of porous media are influence by the pH and ionic strength (IS) [10,16–18]. As the pH of TNPs approached the point of zero charge (pH_{pzc}) of TNPs, their aggregates size enhanced while their mobility decreased [16]. At or near the pH_{pzc}, the surface ionization of nanoparticles is reduced to zero, thereby decreasing the repulsive forces between nanoparticles and allowing the formation of nanoaggregates. An increase in the IS reduced the magnitude of the electrostatic repulsion resulting in an intensification of the aggregation phenomena [17]. The stability of nanoparticles in natural environments is also affected by the presence of natural organic matter (NOM). Fang et al. [10] reported that aquagenic biopolymers could increase the coagulation rate of colloidal montmorillonite, while fulvic acids were shown to stabilize colloidal solutions. Fang et al. [10] demonstrated that TNPs can have potential to be well dispersed in soil solutions when ISs less than 0.005 M with significant portion of dissolved soil organic matter (SOM) in soil systems.

Dispersion of nanoparticles in the subsurface and groundwater environments involves a higher transport and a greater potential for risk of exposure since well-dispersed nanoparticles will be transported longer distances, and be potentially involved in particle-facilitated contaminant movement [20–22]. In the last few years, several studies have been published on the transport of nanoparticles in porous media [16,23,24] and illustrated that nanoparticles including carbon nanomaterials, anatase, and silica exhibited various transport behaviors. Guzman et al. [16] observed that the mobility of TNPs were enhanced with time as deposition sites became saturated in two-dimensional model of porous structure column. Results of Lecoanet et al. [23] indicated that Darcy velocities could also affect transport and deposition of nanoparticles and an increase in the flow velocity increased the effluent of TNPs [23]. However, most of these experiments were examined in regular porous media, polystyrene bead-packed columns or glass [10] but regular porous media are unable to accurately represent the different of mineral surface types, roughness of granular media, and grain size distributions surface charge heterogeneities encountered in real soil systems. Consequently, the environmental implications of such experiments containing regular porous media were restricted.

Therefore, in this study, TNPs were selected as typical representative of engineering nanoparticles due to the extensive use of TNPs in manufacturing with various characteristics of soils because soil are complicated assemblies of solid, liquids, and gasses [25,26]. Therefore, the first aim of this work was to examine the effect of soil characteristics on stability of TNPs through sedimentations technique and a secondary objective was to estimate how far TNPs could be transported in various soils columns. In addition, the single-collector efficiency was calculated using the classical filtration theory to gain better understanding of particle deposition and maximum travel distance of the TNPs in soil systems.

2. Materials and methods

2.1. Characterization of soils

Four surface (0–20 cm) soils were collected from Maltepe, Kizilay, Beytepe, and Ulus in Ankara, Turkey and hereafter referred to soils MA, KI, BE, and UL, respectively. The sampled soils were air-dried, ground to pass through a 1-mm sieve, and stored in plastic bottles until utilized. Selected physiochemical properties of soils are shown in Table 1. Soil texture was determined using the pipette method. Cation-exchange capacity (CEC) of soil was measured at pH 7.0 using 1 mol/L ammonium acetate. The natural pH of soils was measured in a 1:5 material/water ratio by pH meter (pH/ISE Meter, Model 710 thermo Oriom). SOM was determined by the Walkley–Black combustion method [27]. The soil suspensions used in this work were obtained at a soil to deionized (DI) water ratio of 1:20. Zeta potential (ZP) of soils and soil suspensions in the absence or presence of TiO_2 was determined by Zetasizer Nano S Instrument (Malvern Instrument Ltd, Malvern). IS of soil suspensions were estimated from the simple linear equation of IS and electrical conductivity [28]. Dissolved organic matter (DOM) of soils suspensions determined by total organic carbon analyzer (Apollo 9000, Teledyne Tekmar), after centrifuging and filtering through disposable 0.45-μm membranes. The data of soil suspensions of pH and ZP were shown in Fig. 2.

2.2. Sedimentation experiments

TNPs were purchased from Sigma-Aldrich (Ankara, Turkey) with an anatase purity of 99.7%, specific surface area of 45–55 m^2/g and a primary particle size of 25 nm. TNPs suspensions were prepared in soil solutions according to Fang's method [10]. Briefly, TNPs suspension was prepared by mixing of 1,000 mg of TiO_2 with 25 g of soil with addition of 500 mL of DI water. TiO_2 in DI water at the same ratio in the absence of soil was utilized as control, while soil in deionized water at the equivalent ratio without

Table 1
Selected physicochemical properties of soils

Soil	pH	Soil organic matter SOM (%)	Cation exchange capacity CEC (cmol/kg)	Zeta potential ZP (mv)	Ionic strength IS (mM)	Dissolved organic matter DOM (mg/L)	Texture (%)		
							Clay	Sand	Slit
MA	6.89	5.86	17.5	−20.2	0.84	159.3	15.3	56.7	28
KI	7.76	1.96	9.7	−16.4	0.98	115.7	21.6	32.6	45.8
BE	8.46	2.81	21.6	−15.7	1.63	72.6	15.5	63.4	21.1
UL	8.64	0.19	4.4	−15.5	1.41	97.4	9.9	55.7	34.4

Notes: MA = Maltepe; KI = Kizilay; BE = Beytepe; UL = Ulus.

TiO_2 was used as blank. After 24 h shaking, mixtures were transferred into 1-L beaker and allowed to settle undisturbed for 8 d. Aliquots of all suspensions were taken from the top of the beaker at each time interval and the concentration of TNP was monitored. Analysis of TiO_2 nanoparticles was performed after completely dried suspension aliquots was digested in H_2SO_4/NH_4SO_4 solution using an inductively coupled plasma atomic emission spectroscopy. The average aggregate size of stable TNPs determined using a laser particle analyzer (SALD-7500nano, Shimadzu). The stable TNP suspensions in DI water after 8 d were collected for used of column experiments. Although numerous nanomaterials are formed with solid-phase dimensions <100 nm, nanoparticles often form much larger aggregates in the solution where most of these larger aggregates are deposited from suspension [29]. However, stable suspensions of nanomaterials are easily transported. Consequently, we select these stable TNP suspensions to investigate the transport behaviors through soil columns. The concentration of TNPs in soil environment is estimated to be at mg/L levels, however, high concentration of TNPs may exist in particular areas, especially in case of the leaking accident of TNPs manufacture industrial unit. Therefore, the consequences of this study can give a worst-case situation for TNPs mobility through soil columns.

2.3. Column breakthrough experiments

Transport behavior of TNPs through the soil porous media was examined through a series of soil column experiments. The glass soil column was used with an inner diameter of 25 mm and a length 20 cm. Firstly, soil column was depolished in the inner wall to make it rough to avoid the preferential flow. Secondly, the column was uniformly packed to a height of 10 cm with air-dried soil and the column initially saturated with DI water. DI water was added from the bottom of the column moving upwards through the whole column length to eliminate any air pockets, and then the saturated soil columns were leached with 100 mL of DI water. After that the absorbance of out flow at 800 nm was measured, and it was found that the absorbance was less than 0.02, suggesting soil colloid in the outflow has been considerably reduced. Following the leaching step, TNP suspensions were pumped onto the top of soil columns and the gravity flow was used for leaching. The constant water head was sustained throughout the experiment and the outflow samples were collected at discrete leaching time intervals for the determination of TNPs concentrations. The average soil collector diameters were determined by the sum of the sand, silt, and clay particles diameters of 0.175, 0.02, and 0.0015 mm multiplied by their respective percentage contents in soil. The pore volume (V_0) of soil columns was determined by weight according to Delolme et al. [30]. Detailed physical parameters of the soil columns are shown in Table 2. During the course of experiment, the TNPs concentration of inflow (C_0) and outflow (C_f) was measured to obtain breakthrough curves of C_f/C_0 as a function of the number of pore volumes passing through the soil columns. All experiments were carried out at room temperature. (20 ± 1℃).

3. Results and discussion

3.1. Sedimentation analysis

Fig. 1 demonstrates the deposition processes of TNPs in the different aliquots of soil suspensions and DI water at the different sampling times. As shown in Fig. 1, soil characteristics have a critical role for the suspensions of TNPs. After settling for 24 h, the relative suspensions of TNPs concentrations were 34 and 32% for soils MA and KI, respectively, which were the comparatively high DOM and low ISs (Table 1) and in DI water was 24% which was lower than above mentioned soils. Afterward, the relative concentration of TNPs suspended showed an abrupt decrease over the initial 2–4 d, and thereafter remained unchanged up to

Table 2
Experiment conditions and column properties

Soil columns	Average soil collector diameter (μm)	Pore volume of columns V_0 (mL)	Column porosity P	Darcy velocity V_d (cm/h)	Pore water velocity V (cm/h)	Dispersion coefficient D (cm^2/h)	Péclet number P_e
MA	105	28.2	0.575	1.82	3.165	14.192	2.23
KI	66	22.5	0.459	5.14	11.198	9.156	12.23
BE	115	23.7	0.483	2.79	5.78	17.33	3.33
UL	104	23.4	0.477	4.48	9.39	41.55	2.26

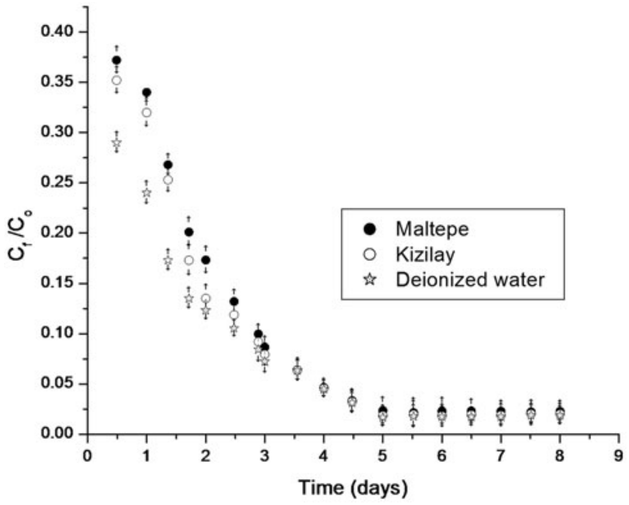

Fig. 1. Sedimentation curves of TiO_2 nanoparticles in Maltepe and Kizilay soil suspensions and deionized water. Error bar for standard deviation.

8 d. On day 8, the suspensions of TNPs were 1.87–2.27% which was equal to 37.5–45.4 mg/L as shown in Fig. 1. For soil suspensions of UL and BE soils with comparatively low DOM and high ISs as shown in Table 1, TNPs settled from solution far more rapidly and after 24 h, the suspensions of TNPs concentrations were 1.5 and 1.2% for soils UL and BE, respectively, and no TNPs were detected in the suspension after settling for 4 d (data not shown).

The suspensions of particles in aqueous solutions required to balance the repulsive forces against van der Waals attractive forces are obtained from the Coulombic repulsion forces deduced from electrostatic double layer repulsions and the steric repulsion forces produced from the adsorption of long-chain charged polymers on the surface of particles [12]. Steric repulsions between two particles result from volume restriction and osmotic effects. The former occurs from the configuration reduction in the zone between particle surfaces; the later arises from the high concentration of adsorbed charged macromolecules in the region between the particles as they come near [12]. Electrostatic and steric repulsion forces reduce aggregation and attachment of particles to soil surfaces [31]. In this study, zero point charge of TNPs was 4.2 and the ZP of TNPs at pH 5.8–8.8 in DI water ranged from −20.72 to −22.46 mV as shown in Fig. 2. The ZP of soil particles ranged from −15.5 to −20.2 mV (Table 1). Thus, it was estimated that repulsion existed between negatively charged TiO_2 particles and soil particles. However, increases in solution IS will reduce the thickness of the electrical double layer and magnitude of the surface charge. Derjaguin–Landau–Verwey–Overbeek (DLVO) [32,33] theory predicts that NP aggregation and retention will increase with IS due to a reduction in the height of the repulsive energy barrier and an increase in the depth of the secondary minimum. Therefore, higher IS of soils UL and BE could elucidate the fast settling of TNPs. However, Fang et al. [10] reported that particles containing grafted surfactant make another mechanism of

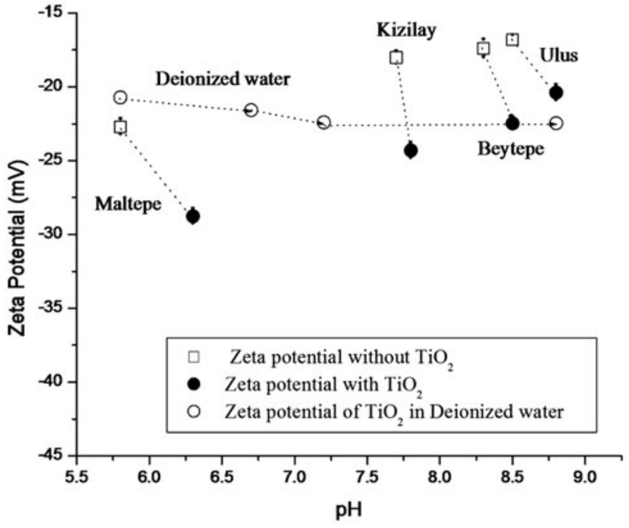

Fig. 2. ZP of soil suspensions with (●) and without (□) TiO_2 nanoparticles as a function of soil suspension pH. ○ represents ZP of TiO_2 nanoparticles in deionized water.

stabilization, referred to as steric stabilization. Since the molecules of DOM solubilized in DI water can act as a kind of surfactant reducing the collision and agglomeration between nanoparticles, thus giving a sterically stabilized system. Therefore, comparatively higher DOM content of MA and KI soils (Fig. 1) were expected to result in suspension of TiO_2 nanoparticles. This was consistent with the results of Hu et al. [34] demonstrating nanoparticles (Fe_3O_4) are more stable in the presence of high-level humic acid due to much stronger interparticle electrostatic repulsion and therefore a much more stable suspension. This finding is agreed with the mechanism of stabilization of colloidal particles by steric interaction that was demonstrated to be suitable in case of NOM [19,35]. In addition, the ZP of TiO_2 nanoparticles in solution is a function of pH and can be referred to as an indication of the stability of the suspension. When solution pH was higher than zero point charge, ZP of TiO_2 became more negative with increasing pH, which resulted in increased suspension [16]. However, in our experiments, the suspension TiO_2 decreased with an increase soil pH and ZP (Table 1, Fig. 1), suggesting that ZP other than soil suspension pH played a significant role in determining of TiO_2 suspension. The ZP is a significant parameter affecting the magnitude of charge-based interactions of a particle such as electrostatic repulsion of other like charged particles. The ZP disturbs the ionic distribution in the porous medium surrounding it and TiO_2 will be more stable in systems with more negative ZP. The ZP of soils MA and KI in the presence of TNPs was much more negative than those of soils BE and UL, and also much more negative than those of their soil suspensions in the absence of TNPs, hence resulting in more stable suspension of TiO_2 in soil MA and KI suspensions as shown in Fig. 2. These results are consistent with Fang et al. [10] who found that ZP other than soil suspension pH played a important role in determining of TiO_2 suspension in different soils.

3.2. Transport of TiO_2 nanoparticles through soil columns

Results of TNPs transports studies with various soils are shown in Fig. 3. The results are presented in the form of representative breakthrough curves (BTCs), i.e. the fraction of the inflow particle concentration leaving the packed bed, C_f/C_0, as a function of pore volumes.

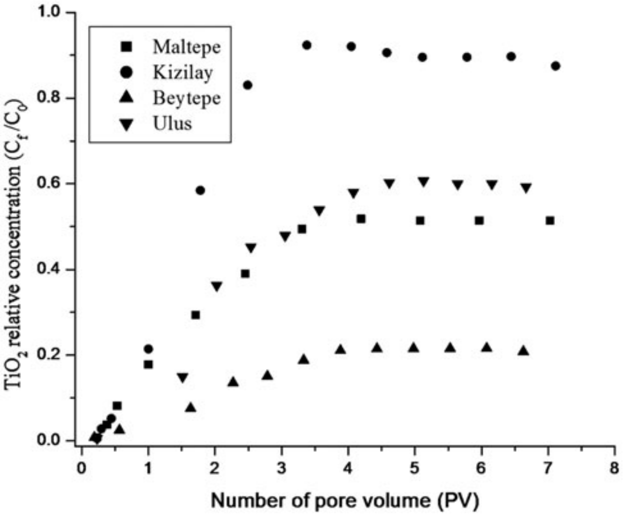

Fig. 3. TiO_2 nanoparticles breakthrough curves in various soil columns.

In soil column of KI, TNPs existence in the first pore volume was approximately 21% of inflow concentrations and final plateau value 90.6% at pore volumes 4–6. For soil MA, the existence of TNPs in the first pore volume was approximately 17.8% of inflow concentrations and final plateau value 51.8% at pore volumes 4–6, which suggests that deposition of TNPs on soil particle surface may contribute to the retention of TNPs for soil MA. ZP of both the TNPs and the soil particles was negative, thus attachment between them is unfavorable according to the classical DLVO theory. However, deposition under unfavorable condition is still possible, as mentioned by Yi and Chen [36]. The soil particles surfaces are generally heterogeneous with both negative and positive sites [37]. In addition, the low Darcy velocity of soil MA as shown in Table 2 was another factor that effects the TNP deposition. It was reported that lower Darcy velocity would result in more capable Brownian diffusion mobility to collector surface [23]. High colloid deposition took place with reducing flow rates [38]. In soil column BE and UL, TNPs tended to enhance slowly with leaching time and achieved the plateau values (C_f/C_0), 21.5 and 60.7%, respectively, as shown in Fig. 3. This experimental result is in analogous with the DLVO theory of particle stability and particle deposition enhanced with IS. The significant concentrations of TNPs were found in the effluent of soils columns of BE and UL even that settling of TNPs was very fast as mentioned in Fig. 1. One possibility for the effluent concentration of TNPs could be the large soil grain diameters in these soils resulting from their high sand content. Larger soil grain diameters are ready to create big pores and shadow zones, where particle deposition would be considerably hindered [39].

The classical filtration theory is used to quantitatively analyze the particle deposition with respect to

Table 3
Experimental results from BTC experiments calculated with classical filtration theory

Soil column	Diffusion η_d	Interception η_I	Gravitational sedimentation η_g	Single-collector contact efficiency $\eta_t = \eta_d + \eta_I + \eta_g$	Attachment efficiency, α	Max. travel L_{max} (cm)	Deposition rate coefficient K_d (h^{-1})
MA	5.77	7.99×10^{-4}	3.02	8.79	1.24×10^{-4}	103.95	0.3643
KI	2.01	2.21×10^{-3}	0.24	2.25	3.98×10^{-5}	625.86	0.2687
BE	5.11	9.75×10^{-4}	2.19	7.30	3.12×10^{-4}	45.03	1.8373
UL	6.72	1.21×10^{-3}	2.95	9.67	6.39×10^{-5}	149.52	0.2799

different transport mechanisms: Brownian diffusion, interception, and gravitational sedimentation. As illustrated by Tufenkji and Elimelech [40], the overall single-collector contact efficiency (η_t) equals to the sum of the single-collector contact efficiency due to diffusion (η_d), interception (η_I), and gravitational sedimentation (η_g) (i.e. $\eta_t = \eta_d + \eta_I + \eta_g$). Following the method of Tufenkji and Elimelech [40], values of η_d, η_I, and η_g were achieved for the tested media and are summarized in Table 3. It shows that Brownian diffusion was the predominant mechanism for the removal of the nanoparticles for all four soils media. In addition, gravitational sedimentation was also played significant role for TNPs removal due to the high density of the TiO_2 nanoparticles. This density influence appears for the soil MA, KI, BE, and UL, where the gravitational sedimentation accounted for 34.36, 10.67, 30, and 30.51%, respectively, of the single-collector contact efficiency. This behavior of TiO_2 nanoparticles is rather different from that of the widely studied latex particles. For example, Zhuang et al. [41] investigated mobility of latex particles in a sand column and observed that gravitational sedimentation was insignificant for removal of particles. The attachment efficiency α, reflecting the fraction of collisions between particles and collectors that result in attachment and deposition rate coefficient (K_d), is then calculated via:

$$\alpha = \frac{2}{3}\frac{d_c}{(1-P)L\eta_t}\ln\left(C_f/C_0\right) \tag{1}$$

$$K_d = \frac{3}{2}\frac{(1-P)}{d_c P}V\alpha\,\eta_t \tag{2}$$

where d_c is the diameter of the spherical collector, P is the porosity of the porous medium, L is the length of the porous medium bed, V is the pore water velocity, and C_f/C_0 is the ratio between the colloid effluent concentration and the colloid influent concentration after the breakthrough curve has reached a plateau. The attachment efficiency (α) and deposition rate coefficient (K_d) were decreased from suspensions in the order of KI < UL < MA < BE, which was the reverse order of the travel distances for these soils, suggesting that large decrease in TNPs from suspensions would a higher deposition rate and collision efficiency by the first-order particle deposition equation as shown Table 3.

Estimate of colloid maximum travel (L_{max}) is another possible indicator of mobility for soil columns. From Eq. (3), the maximum travel distance (L_{max}) in the soil media can be calculated via:

$$L_{max} = \frac{2}{3}\frac{d_c}{(1-P)\alpha\,\eta_t}\ln(C_f/C_0) \tag{3}$$

where L_{max} is defined as the travel distance over which 99% removal of the nanoparticles occurs. Experimental deposition rate coefficient (K_d) values of TiO_2 nanoparticles in the tested soil columns ranged from 0.2687 to 1.8373 and the travel distance of the soil columns are 45.03–625.86 cm, which is farther from a typical surface soil depth of 30 cm, demonstrating severe risks to deeper soil layers or even groundwater.

4. Conclusions

Sedimentation and column experiments were conducted to determine the effect of soil characteristics on the stability of TNPs suspensions in soil solutions as well as their effect on the transport behavior of TNPs in saturated real soil columns. The present work confirmed that the TNPs are stable in soil solutions. The suspensions of TiO_2 relative concentrations were higher for MA and KI soils which had comparatively higher DOM and low IS than those of UL and BE soils. A large decrease in TiO_2 nanoparticles from suspensions results in greater deposition, which is revealed by the attachment efficiency (α). The result is consistent with the prediction by classic DLVO theory. The higher stability of TNPs suspensions resulted in a higher transport of TiO_2. The estimated travel distances of soils MA, KI, BE, and UL ranged from 45.03 to 625.86 cm under saturated homogeneous conditions exceeding 30 cm, a particularly surface soil depth, demonstrating the severe risks to deeper soil layers or even groundwater would potentially occur in these soils.

Acknowledgments

This work is supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under the 2216-International Researchers Fellowship Programmes. The authors would like to thank the anonymous reviewers for their valuable comments and suggestions to improve the quality of the paper.

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