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Transport of TiO_2 nanoparticles and their effects on the mobility of Cu in soil media

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ABSTRACT

The transport behavior of TiO_2 nanoparticles (TNPs) through different soil columns as well as their effects on the mobility of Cu was systematically examined. Results showed that a constant concentration plateau (C_f/C_o%) was achieved at experimental breakthrough curves, ranging from 89%, 53%, and 60% for soils Gölbaşı (Gö), Hacettepe (Ha), and Batikent (Ba) respectively. While Brownian diffusion was the predominant mechanism for TNPs removal in all three soils media, gravitational sedimentation also played a significant role, accounting for 10.58%, 35.52% and 28.84% of the overall single-collector contact efficiency for the soils Gö, Ha and Ba respectively. The estimated travel distances of TNPs in soils ranged from 100 to 593 cm, indicating potential risks of TNPs to the environment and public health. Desorption of Cu from TNPs ranging from 87.57 to 99.08%, demonstrates that TiO_2 nanoparticles-associated Cu may not be stable when released to soil media.

Keywords: Soil pollution; TiO_2nanoparticles; Brownian diffusion; Co-transport of pollutants; Classical filtration theory

1. Introduction

Nanotechnology is rapidly developing as a major economic sector and new applications for nanoparticles are emerging with increasing research and development (R&D). TiO_2 nanoparticles (TNPs), one of the important metal oxide nanoparticles, have extensively been used in many products including sunscreens, cosmetics, paints and solar cells [1,4]. With increasing growth of the production, consumption and disposal of nanomaterials, their release to environmental media is likely to increase [5–10]. TNPs have the potential to be transported to the subsurface and may pollute groundwater [11]. Moreover, TNPs can behave as colloidal carriers for the adsorption of pollutants and increase their mobility in the subsurface and groundwater environments, referred to as "colloid facilitated transport of pollutants" [12]. Therefore, the fate and transport of TNPs in the subsurface is of increasing scientific interest.

Although transport of colloids has been studied for years [13], there has been limited information available on the transport behavior of metal oxide nanoparticles and the effect of their presence on the mobility of heavy metals in soil media. Specifically, studies that explores the mobility of metal oxide nanoparticles using real soil media is lacking. One of the classical studies on the deposition efficiency of Brownian particles was reported in 1990 [14], in which a theoretical framework for deposition kinetics of polystyrene latex particles (46–753 nm) on glass beads was presented. Another early study by Kretzschmar and Sticher [15] investigated the mobility of humic acid-coated hematite particles (122 nm) in soil media. These studies concluded that the presence of humic acids and Ca^{2+} in the medium can influence the mobility and deposition kinetics of nanoparticles. Cheng et al. [16] examined column

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breakthrough behaviors of C_{60} nanoparticles through a Lula soil. Liu et al. [17] investigated the deposition behavior of boron nanoparticles in quartz sand. A common conclusion of these studies was the flow-rate dependency of deposition of colloids. Zhuang et al. [18] concluded that amphiphilic colloids are likely to be more mobile than other colloids and suggested further exploration of the effects of size and surface properties in predicting mobility of colloids in porous media. Compared to the number of studies on the mobility of non-metallic nanoparticles and other nanostructures, the number of studies on metallic nanoparticles is relatively scarce. One of these few studies belongs to Guzman et al. [19], mobility of TNPs in porous media. The authors concluded that solution pH and surface potential of TNPs play a significant role in interactions of nanoparticles with each other and with the surface of porous media. Lecoanet and Wiesner [20] explored the influence of flow on the mobility and deposition of four metal oxide nanoparticles including magnetite (Fe_3O_4), copper oxide (CuO), titanium dioxide (TiO_2) and zinc oxide (ZnO) in a media constructed using spherical glass beads. It was reported that ionic strength, humic acid, flow rate and solution pH play a critical role in nanoparticle mobility [21]. Existing studies on nanomaterials mobility in porous media were usually conducted in well-defined porous media, glass or polystyrene bead-packed columns and thus do not represent the variety of diverse mineral surface types, surface charge heterogeneity, roughness of granular media and organic matter in real soil systems [22].

In addition, little attention has been paid to the effect of nanoparticles on the mobility of pollutants in real soil media to date. Transport distances of various pollutants are known to be greatly increased when they are associated with mobile colloids [23,24]. The co-transport phenomenon occurring in real soil media in the presence of nanostructure has attracted considerable attention in recent years, specially for nanoscale colloids such as buckminsterfullerene [25] and TNPs [26]. TNPs may alter the transport and fate of common environmental metal pollutants such as Cu, by dramatically affecting their distribution between mobile and immobile phases [26]. Tungittiplakorn et al. [27] observed that amphiphilic polyurethane nanoparticles increased the mobility of pollutants in soil media with their hydrophobic interior region and hydrophilic surface. Hofmann and von der Kammer [28] reported that carbonaceous engineering nanoparticles (ENPs) facilitate the mobility of hydrophobic organic pollutants in porous media carbonaceous ENPs may act as carriers for organic pollutants.

In order to study transport in real soil media and explore co-transport of pollutants, TNPs were selected as typical representatives of engineering nanoparticles due to the extensive use of TNPs. Soil samples were collected from three locations in Ankara, Turkey as soil may be both a "sink" and/or "source" of metallic and organic. Its properties such as grain size, surface area of the grains, their charge, types of minerals and organic matter greatly affect the aggregation and mobility of nanoparticles [29]. The objectives of the current study were to i) examine the transport behavior of TNPs in saturated soil columns packed with real soil media that have varying characteristics through classical filtration theory; and ii) explore how TNPs affect the transport of Cu in soil media and to determine whether TNPs associated with pollutants such as Cu may pose a greater threat due to enhanced pollutant migration.

2. Colloids transport theory

As part of this study, the theoretical framework originally developed to investigate colloidal transport in porous media was used to examine the transport of TNPs through saturated soil columns. The mean particle sizes of the nanoaggregates in this study are within the submicron range. Therefore, we can characterize TNPs as miniature colloids. Similar treatment i.e. studying nanoparticle aggregates as colloids is prevalent in the literature [27]. Tufenkji and Elimelech [30] formulated a correlation equation to estimate the single-collector contact efficiency for physico-chemical filtration in saturated porous media. The theoretical approach takes into account colloid deposition on soil grains as a result of colloid transport to the non-mobile surface collector (i.e. soil grain) followed by attachment [30]. Colloids transport in porous media can be described by three mechanisms: 1) direct interception of the particles with the media, 2) sedimentation due to gravity, and 3) diffusion due to Brownian motion [31]. Under steady saturated flow conditions, the transport of colloids through porous media can be depicted by a convective–dispersive transport equation including a term for first-order particle deposition [29]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V_P\frac{\partial C}{\partial x} - kC \tag{1}$$

where C is the colloid concentration in solution, t is the elapsed time, x is the travel distance, D is the dispersion coefficient of colloid, V_p is the average travel velocity of particles and k is the particle deposition rate coefficient. Assuming first-order deposition kinetics, colloidal transport is evaluated by the single-collector contact efficiency (η_t) given by as [30]:

$$\eta_t = \eta_d + \eta_I + \eta_g \tag{2}$$

where η_d represents the transport by diffusion, η_I is the transport by interception and η_g is the transport by gravitational sedimentation. The attachment efficiency α,representing the fraction of collisions between colloids and collectors that result in attachment can then be estimated using the following equation:

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

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_d is the Darcy velocity and C_f/C_0 is the ratio between the colloid effluent concentration and colloid influent concentration after the breakthrough curve has reached a plateau. The maximum distance (L_{max}) that colloids may be transported in saturated porous media can be estimated as the travel distance over which 99% removal from the pore solution occurred, L_{max} is expressed as:

$$L_{max} = \frac{2}{3}\frac{d_c}{(1-P)\alpha\eta_t} ln\ (C_f / C_0) \tag{4}$$

where C/C_0 is 0.001.

3. Materials and methods

3.1. Characterization of soils and TiO_2 nanoparticles

Soils (0–20 cm) were collected from Hacettepe, Gölbaşıand Batikent in Ankara, Turkey, hereafter referred to soils Ha, Göand Ba, respectively. Sample soils were air-dried, grounded to pass through a 1-mm sieve, and stored in plastic bottles until utilized. Selected physiochemical properties of soils are shown in Table 1. The natural pH of soils was measured in a 1:5 material/water ratio by pH meter (pH/ISE Meter, Model 710 thermoOriom). Soil organic matter (SOM) was determined by the Walkley–Black combustion method [32]. Soil texture was determined by sedimentation method. Cation exchange capacity (CEC) of soil was measured at pH 7.0 using 1 mol L^{-1} ammonium acetate. Zeta potential (ZP) of soils was measured by a Zeta-Meter System 3.0+. Ionic strength (IS) of soils was estimated from the simple linear equation of ionic strength and electrical conductivity [33]. The concentration of Cu was determined by graphite furnace atomic absorption spectrometry (GFAAS) after digestion in concentrated HNO_3. Dissolved organic matter (DOM) of soils was determined by total organic carbon analyzer (Apollo 9000, Teledyne Tekmar), after centrifuging and filtering through disposable 0.45 μm membranes.

TNPs were purchased from Sigma-Aldrich (Ankara, Turkey) with an anatase purity of 99.7%, specific surface area of 45–55 $m^2 g^{-1}$ and a primary particle size of 25 nm. TNPs suspensions were prepared in soil solutions according to Fang's method [11]. Briefly, TNPs suspension was initially prepared by mixing 1000 mg of TiO_2 with 500 ml of deionized (DI) water by vigorously rotating for 24 h on a rotary suspension mixer, and then transferring it into beakers which were allowed to settle undisturbed for 10 days. The supernatant from the beakers that contained unsettled TiO_2 nanoparticles suspensions were collected after 10 days and used for sorption and leaching experiments. The concentration of TiO_2 nanoparticles in supernatant suspensions calculated with Ti determination by GFAAS was 37.5 mg L^{-1}. The average agglomerates size of TiO_2 nanoparticles colloids determined by ZetaSizer Nano Series Instrument (Malvern Instrument Ltd.) was 250 nm (n = 3). Nanoparticles often form large aggregates with solid-phase dimensions >100 nm in the solution and these large aggregates are deposited from suspension [9]. However, stable suspensions of nanomaterials are easily transported. Consequently, we select these stable TNPs suspensions to investigate transport behavior through soil columns. The concentration of TNPs in the soil environment is estimated to be at μg L^{-1} *l*evels, however, high concentration of TNPs may exist in particular areas, specifically in the case of a chemical accident of TNPs manufacture industrial facilities. Therefore, the results of this study represent a worst-case scenario for TNPs mobility through soil columns.

3.2. Column breakthrough experiments

Transport behavior of TNPs through the soil porous media was examined through a series of soil column experiments. The column system used in this study was the same as that Fang's [11]. Briefly, a glass soil column with a length 20 cm and inner diameter of 2.5 cm was firstly 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 initially saturated with DI water. DI water was added from the bottom of the column steadily moving upwards through the whole column length to eliminate any air pockets, and then saturated soil columns were leached with 100 mL DI. The absorbance of effluent at 800 nm was measured, the absorbance was less than 0.02 suggesting soil colloid in the effluent has been considerably decreased. Afterward, TNPs suspensions were pumped onto the top of soil columns (about 400 mL, 37.5 mg L^{-1}) and the gravity flow was used for leaching. The constant water head was sustained throughout the experiment and effluent samples were collected at discrete leaching time intervals for the determination of mobility of TNPs. The average diameter of soil collector was determined by summation of the average particle diameter of sand, silt and clay (0.175, 0.02 and 0.0015 mm) multiplied by their respective percentage contents in the soil and divided by 100. The pore volume (V_0) of soil columns was determined by weight according to Khan et al. [34]. Detailed physical parameters of the soil columns are presented in Table 2. During the

Table 1
Selected physicochemical properties of soils

Soil type	pH	SOM (%)	CEC (cmol/kg)	Zeta potential (mv)	IS (mM)	DOM (mg/L)	Soil Cu (mg kg^{-1})	Texture (%)		
								Clay	Sand	Slit
Ba	8.74	4.86	3.92	–16.17	1.03	6.70	7.32	12.30	54.50	33.20
Gö	7.34	7.03	8.74	–16.62	0.59	10.10	19.82	25.30	32.0	42.20
Ha	7.11	6.94	15.53	–22.19	0.43	28.70	24.23	18.50	54.20	27.30

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)	Pe´clet number (P_e)
Ba	102.20	28.31	0.577	4.41	7.64	2.27
Gö	64.82	23.45	0.478	5.15	10.77	12.99
Ha	100.59	33.02	0.673	1.75	2.6	2.43

course of experiment, TNPs concentration of influent (C_0) and effluent (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 (22°C).

In the second part of the study, column breakthrough experiments were performed to examine the influence of TNPs on the transport of Cu in the presence or absence of TNPs under saturated flow conditions with the same soil column systems as described above. Cu associated TNPs were achieved by equilibrating TNPs colloids with a known amount of Cu to give final Cu concentrations of 100 µ L^{-1} in TNPs colloids. Preliminary experiment showed that the concentration of TNPs colloids suspensions in the presence of Cu was the same as that in the absence of Cu, suggesting that the addition of Cu did not lead to TiO_2 nanoparticle aggregation. Total concentrations of Cu and TNPs in the influent and effluent of the soil column were determined. Soil columns were leached with 100 µg L^{-1} Cu-spiked TNPs colloids, while soil columns leached with Cu solution of the same concentration but without any TNPs were used as control. Eluted Cu leached by Cu-TiO_2 suspensions was separated into soluble and TiO_2-associated fractions by splitting column effluent into two portions. One portion of the effluent was centrifuged at 15,000 × g for 30 min, and the concentration of Cu in the supernatant aqueous phase was defined as the soluble fraction, while the other effluent portion, which was not centrifuged, was defined as the total Cu concentration. After the digestion of the effluent according to the method of Fang et al. [11], total Cu concentration in the outflow was determined by GFAAS.TiO_2-associated Cu fraction was obtained by subtracting dissolved Cu concentration from total Cu concentration.

3.3. Sorption of Cu on soils and TNPs suspensions

Preliminary experiments were done to estimate the necessary time required to obtain equilibrium for Cu sorption by the tested soils, which could be attained after 24 h. Therefore, an equilibrium time of 24 h was selected in study. All experiments were carried out in triplicate at a constant ionic strength provided by addition of 0.01 mol L^{-1} KCl. Sorption experiments were performed by mixing soil (0.2 g) with 0.01 mol L^{-1} KCl solution (20 mL) containing varying concentrations of Cu (0–100 mg L^{-1}) in 50 mL polyethylene centrifuge tubes. Mixtures were initially adjusted to pH 6.5 with NaOH or HNO_3 and subsequently soil suspensions were shaken on a reciprocal shaker at 200 rpm for 24 h. After that, the suspension was centrifuged at 3500 × g for 20 min and filtered through disposable 0.45 mm pore size polycarbonate filter, and Cu concentrations in the equilibrium aqueous phase were determined by GFAAS. The quantity of Cu adsorbed was calculated by subtracting the equilibrium concentration of the solution from the initial concentration.

For sorption of Cu on TNPs suspensions, TNPs suspensions (37.5 mg L^{-1}, 20 mL) containing varying concentrations of Cu (0–100 mg L^{-1}) were rotated end-over-end for 24 h. when suspensions reached equilibrium after 24 h, the suspension was centrifuged at 15,000 × g for 30 min and Cu concentration in the aqueous phase was determined. Adsorption isotherms were developed according to Freundlich and Langmuir models:

$$\text{Log } q_e = \log k + 1/n \log C_e \tag{5}$$

$$C_e/q_e = C_e/q_m + 1/q_m K_L \tag{6}$$

where q_m is the amount adsorbed in (mg kg^{-1}), C_e is the equilibrium concentration (mg L^{-1}), respectively. K_L is an affinity parameter related to the bonding energy of the surface in the Langmuir equation. k and n are Freundlich constants which are related to adsorption capacity and intensity, respectively.

4. Results and discussion

4.1. Transport of TNPs through soil columns

Results of TNPs transports behavior studies with real soils media from three locations are shown in Fig. 1. 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.

For experiments with soil column containing soil from Gö location, TNPs existence in the first pore volume was approximately 23% of initial concentration and the final plateau value was 89% (C_f/C_0) of inflow concentration at pore volumes corresponding to the range of 3–6. For soil Ha the existence of TNPs in the first pore volume was approximately 21% of inflow concentrations and final plateau value 53% of influent concentration corresponding to pore volumes of 3–6, Lower plateau value than soil Gö suggests that deposition of TNPs on the surface of soil grains is a dominant mechanism resulting in retention of TiO_2 nanoparticles for soil Ha. As zeta potential of both TNPs and soil grains are negative, thus attachment between them is unfavorable according to the classical Derjaguin, Landau, Vervey, and Overbeek (DLVO) theory [35]. However, deposition under unfavorable conditions is still possible, as stated by Yi and Chen [36]. Soil particle surfaces are generally heterogeneous with both negative and positive sites [37]. These positive or

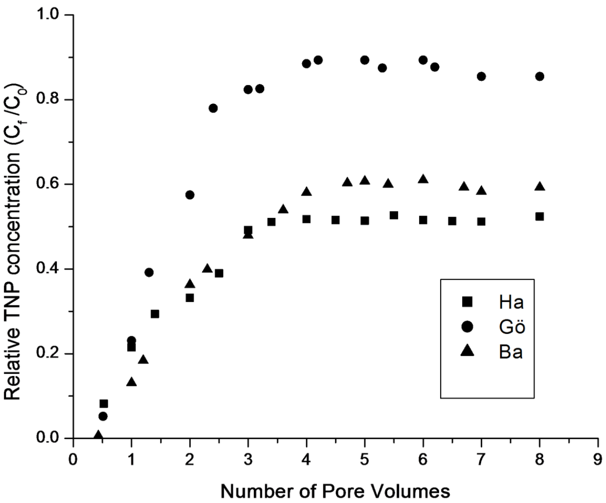

Fig. 1. TNPs breakthrough curves in various soil columns.

less negative sites will be locally favorable for TNP deposition (or adsorption), hence the presence of these sites is one factor that leads to deposition onto soil grain surfaces. Low Darcy velocity of soil Ha as shown in Table 2, is another factor that affects the degree of TNPs deposition. Lower Darcy velocity results in an increase in Brownian diffusion-induced mobility to collector surface [38]. For soil column Ba, TNPs a slow transport through the soil column was observed reaching a final plateau value of 60% as shown in Fig. 1. This experimental result is in accordance with DLVO theory of particle stability and particle deposition enhance with ionic strength. However, significant concentrations of TNPs were found in the effluent of soil column of soil Ba. As soil Ba has high sand content (54.5%), its grain diameter is large. Larger soil grain diameters implicate larger pores and shadow zones than soils containing clay and silt. The presence of large pores and shadow zones through the soil column hinder particle deposition considerably [39].

Estimates of colloid maximum travel (L_{max}) and deposition rate coefficient (K_d) provide measures of a colloids' mobility (Table 3). Gravitational sedimentation played a significant role for TNPs removal due to the high density of TNPs. Effect of density on mobility was observed for all soil samples. For soils Ha, Gö and Ba, gravitational sedimentation accounted for 35.52%, 10.58% and 28.84% of the single-collector contact efficiency respectively. This behavior of TNPs is contrary to findings of other studies in the literature. For example, Zhuang et al. [18] investigated mobility of latex particles in a sand column and observed that gravitational sedimentation was insignificant for removal of particles. Experimental K_d values of TNPs in soil columns ranged from 0.12 to 0.38. The mobility indices L_{max} of soil columns range between 100 and 593 cm, which is greater than a typical surface soil depth of 30 cm [40], indicating pollution of deeper soil layers and potentially groundwater.

4.2. Copper sorption onto soils and TNPs

Fig. 2 shows equilibrium isotherms of Cu sorption onto soil and TNPs. The amount sorbed increased with an increase in equilibrium Cu concentration and all columns achieved a plateau value at a high equilibrium Cu concentration. This explains the higher adsorption at lower concentrations, which then reduces as concentration increases as available vacant adsorption spots decrease [41].

Two common adsorption models including Langmuir, and Freundlich were used to examine adsorption mechanism. Table 4 shows predicted model constants of the Langmuir and Freundlich isothermal equations. The Langmuir model was found to be the best fit with the test data with the highest correlation coefficient (r^2). The overall adsorption capacity of soils follows the order Ha > Ba > Gö.

The sorption capacity of Cu on soils mainly depends on pH, clay mineral and carbonate contents, DOM and CEC of the soil [41]. It was reported that DOM has a critical role in sorption of Cu to soils. High DOM always results in high sorption affinity for Hydrophobic Organic Contaminants (HOCs) [26,41]. Therefore, soil Ha with comparatively higher DOM content than soils Gö and Ba has the highest Cu sorption capacity. However, DOM may also exhibit different sorption features for HOCs depending on its origin [40]. For soils containing only a very small amount of

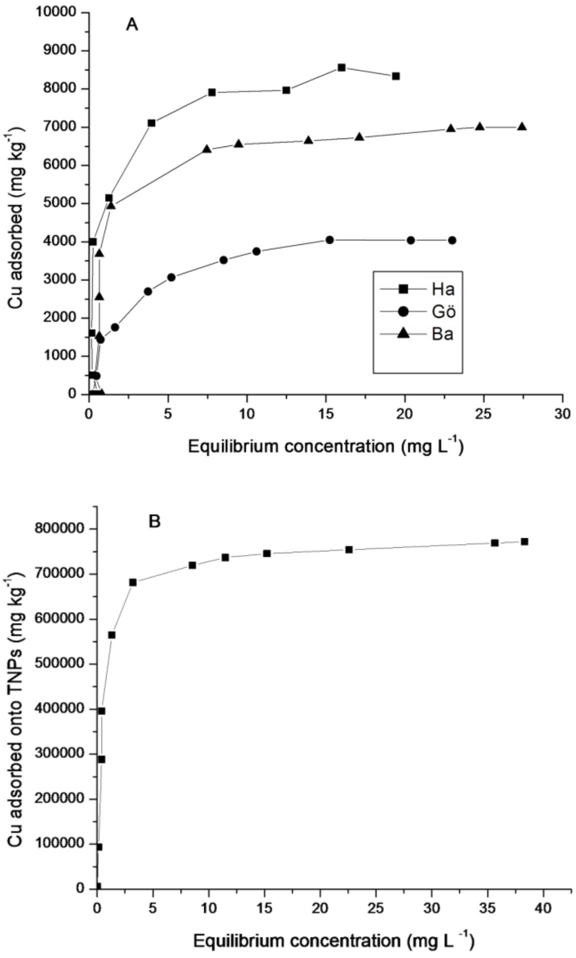

Fig .2. Sorption isotherm of Cu for the soils (A) and TNPs (B).

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

Soil columns	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})
Ba	5.65	7.50×10^{-4}	2.29	7.94	1.02×10^{-4}	137	0.3851
Gö	1.86	1.66×10^{-3}	0.22	2.08	4.64×10^{-5}	593	0.1255
Ha	4.60	4.90×10^{-4}	2.54	7.15	1.81×10^{-4}	100	0.1636

Table 4
Predicted isothermal constants of Cu and TNPs by Freundlich and Langmuir isotherms

Materials	Langmuir equation			Freundlich equation		
	q_m (mg kg^{-1})	K_L	r^2	1/n	K	r^2
Ha	8865.25	0.89	0.99	0.406	3090.29	0.69
Gö	4592.50	0.39	0.99	0.452	1230.28	0.86
Ba	7518.80	0.52	0.98	0.399	2290.87	0.67
TiO_2 nanoparticles	785389.61	1.30	0.99	0.494	229086.77	0.77

Table 5
Sorption and desorption of Cu on TNPs in influent and effluent samples

Soils	Inflow			Outflow		
	Total Cu in TNPs suspensions (μg L^{-1})	Cu sorbed on TNPs (mg g^{-1})	Dissolved Cu in the solution (μg L^{-1})	Cu sorbed on TNPs (mg g^{-1})	Cu desorbed from TNPs (%)[a]	Soluble Cu (%)[b]
Ba	100	2.71	5.80	0.337	87.57	7.75
Gö	100	2.71	5.80	0.061	97.70	81.00
Ha	100	2.71	5.80	0.025	99.08	58.56

[a] Amount of Cu desorbed from TNPs in outflow compared to Cu on TNPs in inflow. [b] Amount of Cu soluble from TNPs in the outflow compared total Cu associated with TNPs in the outflow.

DOM, adsorption of HOCs onto clay surface is the dominant mechanism of adsorption [42]. As soils Gö and Ha have significantly higher organic matter content than soil Ba, there was a stronger interaction between Cu and soil organic matter. However, pH is also an important factor influencing the adsorption affinity of Cu on soils, which is significantly enhanced as solution pH increases [43]. Larger adsorption capacity of Cu on soil Ba compared to Gö may partially be explained by higher pH of soil Ba, though soil mixtures were readjusted four times to pH 6.5 during sorption processes.

Nanoparticles, particularly those possessing highly negatively charged surface, have a high affinity for Cu due to their large surface area [44]. Karathanasis [44] reported that when the sorption capacity of colloid for pollutants is larger than that of the soil matrix, colloid-associated transport likely resulting in greater mobility. In this study, the adsorption capacity of Cu onto TNPs was approximately two orders of magnitude greater than the capacity of soil matrices (Table 4), demonstrating that TNPs has the potential for preferential sorption of soluble Cu resulting in an increased transport of Cu through soil media.

4.3. Transport of TNPs associated with copper through soil columns

Total concentration of Cu was 100 μg L^{-1} in the influent TNPs suspension and the amount of Cu sorbed on TNPs was 2.71 mg g^{-1} (Table 5). As shown in Fig. 3, the breakthrough of Cu in the presence and absence of TNPs varied significantly with soils.

For soil Ba (Fig. 3), 60.55% relative concentration of Cu was observed in the effluent in the presence of TNPs at pore volume 8, which was significantly higher than 1.36% in the case of the absence of TNPs indicating a 59% increase in the mobility of Cu in the presence of TNPs. The result is in line with existing research that nanoparticles enhance the mobility of heavy metal pollutants. 0.337 mg g^{-1} Cu was associated with TNPs in the effluent (Table 5), which indicates that TNPs acted as Cu carrier in the co-transport process. For soil Gö (Fig. 3), TNPs-facilitated Cu transport was insignificant. In the presence of TNPs, the total eluted Cu was just a little higher than that of the control after two pore volumes. The soluble Cu in the effluent was more than 81% of the total eluted Cu, suggesting that Cu was mainly transported in a soluble form. As shown in Table 5, only 0.061 mg g^{-1} of the total Cu was transported with TNPs acting as a carrier for soil Gö. For soil Ha, TNPs exerted almost no facilitated transport of Cu. Low concentrations of Cu were detected in the outflow in the presence and absence of TNPs and TNPs -associated Cu in the outflow was 0.025 mg g^{-1} (Table 5). Soils Gö and Ha have significant concentrations of DOM and it is likely that Cu-DOM complex formation is the dominant mechanism of adsorption and transport for these soils that facilitates the transport of Cu rather than TNPs. Concentration of DOM is a major factor in the degree of enhancement of mobility by nanoparticles.

Existing research in the area shows that during the transport of colloids in soils, pre-sorbed pollutants could be partially or completely “stripped” off from colloids and subsequently sorbed by soil components, and the “strip” rate mainly on the sorption affinity of soils [45]. The amount of Cu desorbed from TNPs during transport was calculated based on the difference between Cu sorbed on TNPs in the inflow and those in the outflow (Table 5). The 87.57–99.08% of Cu desorption from TNPs for all three soils indicated that significantly less Cu was recovered on TNPs in the effluent compared with the influent (Table 5), suggesting that during transport Cu was partially or completely “stripped”

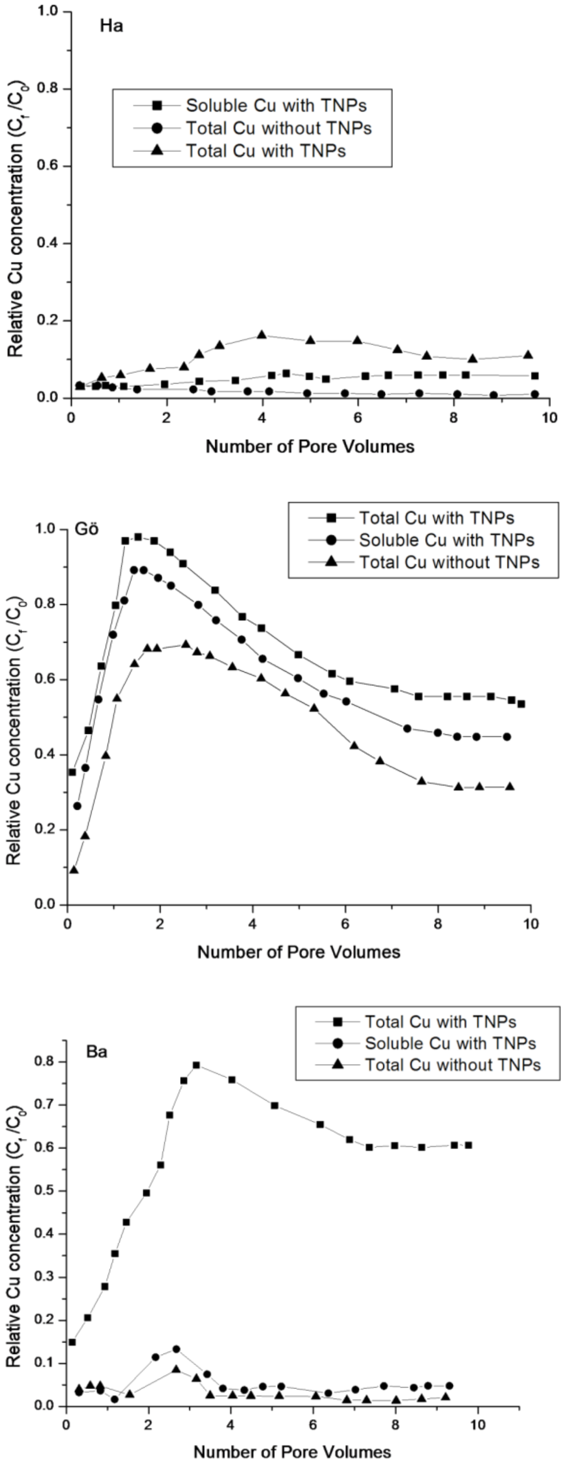

Fig. 3. Breakthrough curves of Cu in the presence or absence of TNPs.

from TNPs to reach equilibrium with the pore water solution and subsequently sorbed by the soil. "Stripping" was a pronounced factor for transport of TNPs with Cu for all three soil samples. The implication of this finding is that TNPs -associated Cu may not be stable when emitted to the soil media and heavy metals pose potential harm to soil and groundwater because of desorption process occurring in soil media as heavy metals transported with nanostructures transfer to the solution and become bioavailable. The result is in accordance with previous studies in the area [45,46].

5. Conclusions

Batch and column experiments were conducted to analyze the transport behavior of TNPs in soil media as well as their effects on the mobility of Cu. The present study provides further evidence that soil properties affect the behavior of TNPs, TNPs-associated Cu transport and sorption of Cu on TNPs and subsequent desorption. DOM, ionic strength and soil pH are major factors affecting mobility of TNPs, transport of TNPs-associated Cu and sorption of Cu through soil media. The estimated travel distances for three soils under saturated homogeneous conditions ranged from 100 to 593 cm that exceeds a surface soil depth of 30 cm, indicating potential pollution of deeper soil layers and groundwater. It was found that TNPs act as carriers for Cu transport in line with previous research in the area. However, Cu was partially desorbed from TNPs during transport, and the degree of desorption ranged from 87.57 to 99.08%, indicating that TiO_2 nanoparticles-associated Cu are not stable when released to soil media and thus pose potential harm to soil and groundwater because of desorption processes.

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