Individual and Co Transport Study of Titanium Dioxide NPs and Zinc Oxide NPs in Porous Media

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Abstract

The impact of pH and ionic strength on the mobility (individual and co-transport) and deposition kinetics of TiO2 and ZnO NPs in porous media was systematically investigated in this study. Packed column experiments were performed over a series of environmentally relevant ionic strengths with both NaCl (0.1–10 mM) and CaCl2 (0.01–0.1mM) solutions and at pH 5, 7, and 9. The transport of TiO2 NPs at pH 5 was not significantly affected by ZnO NPs in solution. At pH 7, a decrease in TiO2 NP transport was noted with co-existence of ZnO NPs, while at pH 9 an increase in the transport was observed. At pH 5 and 7, the transport of ZnO NPs was decreased when TiO2 NPs was present in the solution, and at pH 9, an increase was noted. The breakthrough curves (BTC) were noted to be sensitive to the solution chemistries; the decrease in the breakthrough plateau with increasing ionic strength was observed under all examined pH (5, 7, and 9). The retention profiles were the inverse of the plateaus of BTCs, as expected from mass balance considerations. Overall, the results from this study suggest that solution chemistries (ionic strength and pH) are likely the key factors that govern the individual and co-transport behavior of TiO2 and ZnO NPs in sand.

Introduction

Various studies have shown that TiO2 NPs is toxic to organisms like rats, algae, microbes, invertebrates, and fish. The yearly production of TiO2 NPs is expected to expand to ~2.5 million metric tons by 2025 in the United States alone [1]. Due to their extensive production and use in household and industrial commodities, some of the TiO2 NPs utilized have been discharged into the natural aquatic environment directly or indirectly. Additionally, reports suggest that 10–100 mg/L of Ti is present in municipal wastewater treatment plant effluents [2]. Thus, mechanisms controlling the transport and deposition of these nanomaterials in porous media are critical to understand in order to thoroughly evaluate the mobility and persistence of
these materials in aquatic environments as their bioavailability and toxicity will inevitably be governed by their fate and transport in the environment [3, 4].

The most propitious nanoparticles being identified are ZnO NPs because of their extensive utilization in various industries (e.g. optical and chemical) [5, 6, 7, 8, 9, 10] and commercialized products (e.g. cosmetics) [7, 11, 12]. Yearly production of ZnO NPs has grown over 30,000 tons/year globally [13] mostly due to their diverse applications [14, 15, 16]. Several recent reports have explained that ZnO NPs can cause apoptosis to mammalian cells [16, 17, 18, 19], acute toxic effect and [20, 21], phytotoxicity to plant roots [22, 23], etc. These applications potentially lead to direct and indirect release of ZnO NPs in the aquatic environment. The potential environmental and health risks of nanoparticles are greatly dependent on their fate and behavior in the natural environment in terms of exposure scenarios [24]. Upon discharge, nanoparticles will get released into soil and groundwater [3]. In order to quantitatively assess the potential ecological risk, it is extremely imperative to understand the transport and distribution of ZnO NPs in natural porous media system.

Substantial studies have been done previously on transport and retention of TiO2 NPs and ZnO NPs in porous media [25]. These studies mainly concentrate on the transport and retention of one kind of nanomaterial, either TiO2 or ZnO NPs in porous media. Owing to their various applications in a broad variety of fields, there is increased probability for the conjoint entry of different classes of nanomaterials in nature. Various studies on the co transport of materials like clay, virus, and bacteria, (that did not particularly deal with engineered nano materials) have been reported in recent years, and it was shown that co transport behavior was more complicated than that of individual constituents, stipulating the necessity to evaluate the co transport of nanoparticles [26, 27].

Therefore, the aim of this work was to study the individual and co transport behavior of TiO2 and ZnO NPs, which has a wide range of applications under a series of ionic strengths (0.1–10 mM NaCl, 0.01–0.1 mM CaCl2) and pH (5, 7, and 9). The breakthrough curves (BTCs) and retention profiles of both TiO2 NPs and ZnO NPs were compared with individual transport study. The current study showed the effect of co transport of nanoparticles at different pH and ionic strengths. The packed column experiments were performed over a series of environmentally relevant ionic strength in both NaCl (0.1–10 mM) and CaCl2 (0.01–0.1 mM) and at pH (5, 7, and 9). Transport of only TiO2 NPs was observed to be relatively low at pH 5, whereas, higher BTCs were observed at pH 7 and 9. However, the transport of TiO2 NPs in the presence of ZnO NPs was almost similar to those without ZnO at pH 5, but at pH 7, the presence of ZnO NPs showed a decrease in TiO2 NP transport as indicated by the BTCs. The co presence of ZnO NPs in suspensions increased the transport of TiO2 NPs in sand at pH 9. On the other hand, ZnO NP transport in sand at pH 5 and 7 was less because of the attractive force between sand and NPs. At pH 9, the transport of ZnO NPs increased in sand because of similar zeta potential values for sand and NPs. ZnO NPs in the co presence of TiO2 NPs in suspension showed a decrease in transport than that of those without TiO2 NPs at pH 5. However, at pH 7, the co presence of TiO2 NPs in ZnO NP suspension unveils increase in transport of NPs. The transport in co presence of TiO2 NPs at pH 9 showed an increase in ZnO NP transport under all examined ionic strength. The retention profiles were the inverse of the plateaus of BTCs, as expected from mass balance considerations. The results from this study strongly suggest that the solution chemistries (ionic strength and pH) are likely to play an important role in the individual and co transport characteristics of TiO2 and ZnO NPs in sand. This study is the first of its kind to evaluate the co transport of two very important commercially used nanomaterials, TiO2 and ZnO NPs, which possess substantial environmental risks also.
Materials and Methods
Preparation of TiO₂ NPs and ZnO NP suspension
Titanium dioxide nanoparticles powder (TiO₂ anatase, less than 25 nm in diameter, purity greater than 99.9%) and ZnO NPs (less than 100 nm) were purchased from Sigma-Aldrich Corp. TiO₂ nanoparticle stock suspension (100 mg/L) was prepared by suspending TiO₂ nanopowder in Milli-Q water and sonicating using an ultrasonic processor (Sonics., USA) of 130 W, for 10 min. The aqueous suspensions of ZnO NPs were prepared by suspending ZnO nanopowder in Milli-Q water and sonicating in a bath sonicator for 10 min at 530 W, for 20 min (Crest Ultrasonics). As the nanoparticles, sand, and other chemicals used in the experiment were procured, no specific permissions were required from anywhere. All the tests were carried out within the laboratory, and due care was taken not to contaminate the environment.

For both individual nanoparticles transport and nanoparticles co-transport experiments, the influent concentrations of TiO₂ NPs and ZnO NP suspensions were maintained to be 10 and 5 mg/L, respectively. The ionic strengths of nanoparticles suspensions ranged from 0.1 to 10 mM in NaCl solutions and 0.01 to 0.1 mM in CaCl₂ solutions. The suspension pH was set to be 5, 7, and 9 by adjusting with 0.1 M HCl or 0.1 M NaOH. The zeta potentials and particle sizes of nanoparticles under these conditions were measured using Brookhaven Instruments Corporation, USA. The measurements were performed at room temperature (25°C) and repeated several times.

Porous Media
Quartz sand (CAS Number 14808-60-7, Sigma-Aldrich) was used as the porous media for all nanoparticle transport experiments. The protocol for cleaning the sand was followed as explained by Li et al. [28]. The zeta potentials of the crushed quartz sand were also measured in NaCl/ CaCl₂ solutions under the experimental conditions.

Column Experiments
The cylindrical glass columns (10-cm long and 2-cm inner diameter) were wet-packed with cleaned quartz sand. Briefly, prior to packing, the cleaned quartz sand was rehydrated by boiling in Milli-Q water for at least 1 h. After the rehydrated quartz sand was cooled, the columns were packed by adding wet quartz sand in small increments (~ 1 cm) with mild vibration of the column so as to reduce any layering or air entrapment [29]. The gravimetrically measured bed porosity was approximately 0.40. The approximate porosities of TiO₂ NPs, ZnO NPs, and sand were 0.0065, 0.038, and 0.00019, respectively (Micromeritics, TriStar III, USA). The temperature was 27 ± 5°C throughout the experiment. The absorbance of ZnO and TiO₂ nanoparticles were taken at 370 nm and 330 nm, respectively. The dielectric constant of sand column was estimated according to the formula: \( \varepsilon_r = \frac{\Sigma \varepsilon_i (\varepsilon_i)^0.5}{2} \) [30]. The dielectric constant values for TiO₂ and ZnO NPs with sand were 400.96 and 399.99. On the other hand, the dielectric constant values for TiO₂ and ZnO NPs without sand were 100 and 3.68, respectively [31,32].

The columns were pre-equilibrated with at least ten pore volumes of NaCl /CaCl₂ solutions maintained at a desired ionic strength and pH after packing. Following pre-equilibration, three pore volumes of nanoparticle suspensions were passed into the column, followed by recovery with five pore volumes of NaCl/ CaCl₂ solution at the same ionic strength and pH. The solutions were injected into the columns in a down-flow mode using a peristaltic pump. During the column experiments, the input nanoparticle suspensions were periodically sonicated to evade any settlement of nanoparticles and to sustain the stability of the suspension at desired solution chemistries. The transport experiments were conducted at three ionic strengths (0.1, 1, and...
10 mM) in NaCl and (0.01, 0.05, and 0.1 mM) CaCl$_2$ solutions, at three pH conditions (pH 5, 7, and 9). The pore water velocity of all experiments was set to 8 m/day (0.69 mL/min) in order to represent the fluid velocities in coarse aquifer sediments [33,34].

The column effluent samples were collected (~ 15 mL) in centrifuge tubes at pre calculated time intervals. Following the transport experiment, the sand was taken out from the column under gravity and disjoint into 10 segments (each 1 cm). To release the nanoparticles from quartz sand, approximately 5–10 mL of 0.1 M NaOH/CaCl$_2$ solution was added to each sediment segment, and the mixture was continuously shaken at 300 rpm overnight, and then manually shaken vigorously for a few seconds [35]. The effluent samples and supernatant samples from the recovery of retained TiO$_2$ NPs were analyzed using a UV spectrophotometer (U2910, Hitachi, Japan), whereas the corresponding samples for ZnO NPs were evaluated by UV spectrophotometer (U2910, Hitachi, Japan). The area under the breakthrough elution curve was integrated to provide the percentage of nanoparticles that evacuated the column. The percentage of nanoparticles retrieved from the sediment was obtained by adding the quantity of nanoparticles retrieved from all segments of the sediment and dividing by the total amount of nanoparticles injected. The sum of the percentages of retained particles and particles that exited the column represented the overall recovery (mass balance) of nanoparticles. The mass recovery of nanoparticles for each experiment is provided in the S4–S7 Tables.

Characterization of transport and transported material

**Transmission electron microscopy (TEM).** Size and morphology of individual nanoparticles (TiO$_2$ and ZnO NPs) before and after transport in porous media were characterized using transmission electron microscopy (Technai G2 spirit biotwin (120kv), FEI Company). Samples were collected in 15-ml centrifuge tube before and after nanoparticle (TiO$_2$ and ZnO NP) transport in porous media at pH 5, 7 and 9 at an ionic strength of 10 mM NaCl. The aerated samples (60°C, 30 min) were then deposited onto the lacey carbon-coated copper grid and subjected to TEM analysis.

**X-ray diffraction patterns.** To characterize the TiO$_2$ NPs, ZnO NPs, and sand, X-ray diffraction analysis was carried out using the X-ray Diffraction spectrophotometer (Bruker, D8 Advance, Germany). TiO$_2$ NPs, ZnO NPs, and sand powder were grinded to a make a fine powder, and a uniform smear was prepared on a glass slide. The prepared sample was packed into a sample container for analysis. The crystalline structure of TiO$_2$ NPs, ZnO NPs, and sand were determined with the diffraction patterns obtained.

**Fourier transform infrared spectroscopy.** The functional interaction between the transport and transported material was investigated using FTIR analysis. The nanoparticle samples before and after transport through the porous media were collected and used for analysis.

**Statistical analysis**

All experiments were carried out in triplicates and the data are given as mean ± standard error. The data were processed using Student’s t-test with a p value < 0.05.

**Conductivity Measurement**

Conductivity was evaluated for both the nanoparticles (ZnO NPs and TiO$_2$ NPs) under a series of ionic strengths in both NaCl (0.1, 1, and 10 mM) and CaCl$_2$ (0.01, 0.05, and 0.1 mM) solutions at three different pH conditions, 5, 7, and 9, before and after transport through the porous media. After transport, the samples were collected, and the conductivity was measured using conductivity meter (ELICO, CM 180).
Results and Discussion

Effect of ZnO NPs on TiO2 NP Transport in sand column

The transport of TiO2 NPs in absence and presence of ZnO NPs in sand was examined under a series of ionic strengths in both NaCl (0.1, 1, and 10 mM) and CaCl2 (0.01, 0.05, and 0.1 mM) solutions at three different pH conditions, 5, 7, and 9. The breakthrough curves of TiO2 NPs without ZnO NPs are presented in Figs 1, 2 and 3. The zeta potential of TiO2 NPs was positive; however, the zeta potential of bare sand was negative in both the NaCl (0.1, 1, and 10 mM) and CaCl2 (0.01, 0.05, and 0.1 mM) solutions at pH 5 (S1 and S3 Tables). Therefore, an attractive electrostatic interaction was expected between TiO2 NPs and sand under the examined pH 5 for all ionic strengths. As a result, under all ionic strengths [NaCl (0.1, 1, and 10 mM); CaCl2 (0.01, 0.05, and 0.1 mM)] at pH 5, TiO2 NPs were retained in sand and very less amount of NPs had eluted out. This indicates that the delivery of TiO2 NPs without ZnO NPs was intensely dependent on pH. Previous reports by Chowdhary et al. and Solvitch et al. supported our findings as these studies also suggested that TiO2 NPs have different zeta potential values at different pH, and thus at disparate pH, the transport of TiO2 NPs varies [36, 37]. Though size and zeta potential for the TiO2 NPs were heterogeneous at different solution conditions, the BTC curves of TiO2 NPs were similar under all inspected ionic strengths (S1 Table). These results demonstrate that the impact of ionic strength on TiO2 transport was least at pH 5.
previous report on the cotransport of TiO$_2$ NPs and C60 NPs by Cai, L et al. also validated that the impact of ionic strength on TiO$_2$ NP transport was least at pH 5 [38]. Additionally, the BTCs of TiO$_2$ NPs in presence of ZnO NPs at pH 5 were nearly equivalent to those without ZnO NPs, under all ionic strengths (NaCl/ CaCl$_2$) (Fig 1). Therefore, these results clearly demonstrated that there were no significant (p > 0.05) changes in the transport of TiO$_2$ NPs in presence of ZnO NPs at pH 5.

Both TiO$_2$ NPs and sand have negative zeta potential at pH 7 (S1 and S3 Tables), and so repulsive electrostatic interaction was expected between TiO$_2$ NPs and sand under the examined pH 7 and ionic strength [NaCl (0.1, 1, and 10 mM); CaCl$_2$ (0.01, 0.05, and 0.1 mM)]. At pH 7, the BTCs obtained for TiO$_2$ NPs without ZnO NPs was higher at low ionic strengths. BTCs were sensitive to solution chemistries as indicated by the decrease in breakthrough plateau with increasing ionic strength. The lower BTCs of TiO$_2$ NPs with increasing ionic strength, as observed at pH 7, were consistent with the lower negative zeta potentials observed at high ionic strengths, and thus agreed with the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Figs 1, 2 and 3) [39]. This theory explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting through an aqueous medium. It integrates the effects of Van der Waals's attraction and electrostatic repulsion due to the so-called double layer of counter ions. Cai L et al. and Chen G et al. also reported that the transport of TiO$_2$ increases with increasing ionic strengths, and thus, agreed with DLVO theory [38, 40]. Fang et al. also reported that the variation in pH also altered both the magnitude and separation distance of the repulsive energy barrier in DLVO interaction [39]. Moreover, breakthrough curves in co-presence of ZnO NPs at pH 7 showed a decrease in TiO$_2$ NP transport. These may be due to charge heterogeneity present in TiO$_2$ NPs, ZnO NPs, and sand. However, the results clearly show that there are no significant (p > 0.05) changes in the transport of TiO$_2$ NPs in presence of ZnO at pH 7.

At pH 9, the zeta potential values of TiO$_2$ NPs and sand are more negative than pH 7. Thus, more repulsive electrostatic interaction was expected between TiO$_2$ NPs and sand under the examined pH 9 and all ionic strength [NaCl (0.1, 1, and 10 mM); CaCl$_2$ (0.01, 0.05, and 0.1 mM)] (S1 and S3 Tables). Breakthrough curve of TiO$_2$ NPs at pH 9 was higher than at pH 7. But the BTC plateau in co-presence of ZnO NPs was increased at pH 9 (Fig 3). These results showed that, unlike the negligible change of TiO$_2$ transport induced by the presence of ZnO NPs at pH 5, the copresence of ZnO NPs in suspensions increased the transport of TiO$_2$ NPs in sand at pH 9. ZnO NPs in suspension may compete with TiO$_2$ NPs for deposition sites on sand, contributing to the enhanced transport of TiO$_2$ NPs in sand at pH 9. However no
significant difference (p > 0.05) was noted in transport of individual of TiO₂ NPs when compared to co-transport of TiO₂ NPs with ZnO NPs.

The above results demonstrated that pH plays the most important role in the transport and retention of TiO₂ NPs and ZnO NPs. BTCs of TiO₂ NPs (Figs 1, 2 and 3) at pH 5 were lower in sand due to the electrostatic attraction between sand and TiO₂ NPs (Figs 1, 2 and 3). The electrostatic attraction between sand and TiO₂ NPs at pH 5 has also been reported previously by Cai Li et al. [38]. However, at pH 7 and 9, negatively charged TiO₂ NPs showed repulsion to negatively charged sand, and thereby a decrease in the retention of TiO₂ NPs in sand was noted. The negative zeta potential values of sand and TiO₂ NPs at pH 7 have also been also reported by Dunphy et al. [41]. This observation was true under all ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)].

Effect of TiO₂ NPs on ZnO NP Transport in sand column

The influence of TiO₂ NP copresence in suspensions on the transport behavior of ZnO NPs was examined. The transport experiments of ZnO NPs in packed sand were performed both in the absence and presence of TiO₂ NPs at different ionic strength [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)] and pH conditions (5, 7, and 9). As shown in S2 and S3 Tables, at pH conditions 5 and 7, the zeta potential values of ZnO NPs were positive, but at pH 9, the zeta potential of ZnO NPs was negative. Sand was negatively charged under all examined ionic strength conditions and pH (S3 Table).

The electrostatic interaction between ZnO NPs and quartz sand was attractive at both pH 5 and 7 [41]. At pH 5 and 7, most of the ZnO NPs are retained in the column, and very less amount of ZnO NPs had eluted out. The apparent breakthrough of ZnO NPs in sand was observed under all examined ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)] at both pH 5 and 7 (Figs 4, 5 and 6).

Additionally, ZnO NPs in copresence of TiO₂ NPs in suspension showed decrease in BTC plateau when compared with samples without TiO₂ NPs under all examined ionic strength conditions at pH 5 (Fig 4). From the above results, it was demonstrated that, the copresence of TiO₂ NPs in ZnO NP suspension at pH 5 decreases the transport of ZnO NPs in sand under all examined ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)].

However, the copresence of TiO₂ NPs with ZnO NP suspension at pH resulted in the increase of BTC curve. The zeta potential values of both ZnO NPs and sand were negative at
pH 7 under all examined ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)] (S2 and S3 Tables). Repulsive electrostatic force was expected between ZnO NPs and sand under examined pH 7 and all ionic strength [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)]. BTCs were sensitive to solution chemistries, as indicated by the increase of the breakthrough plateau with increasing ionic strength. However, the difference in individual transport and cotransport was not statistically significant (p > 0.05) at pH 5 and 7.

At pH 9, the BTCs of ZnO NPs obtained was higher at low ionic strength. The lower BTCs of ZnO NPs with increasing ionic strength, as observed at pH 9, were consistent with the less negative zeta potentials observed at high ionic strength, and thus, the results agreed with the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. However, the breakthrough curve in copresence of TiO₂ at pH 9 showed an increase in ZnO NP transport under all examined ionic strength [NaCl (0.1, 1, and 10 mM); CaCl₂ (0.01, 0.05, and 0.1 mM)]. BTCs were sensitive to solution chemistries, as indicated by the increase of the breakthrough plateau with increasing ionic strength. However, the results demonstrated that there are no significant (p > 0.05) changes in the transport of ZnO NPs in presence of TiO₂ NPs at pH 7.

The results from the above studies showed that the co presence of both the NPs (TiO₂ and ZnO) affected the transport of each other at different pH. At pH 5 and 7, the positive charge of ZnO NPs causes the increase in attractive force between sand and NPs, and therefore, the BTCs were decreased. Moreover, the transport of ZnO NPs increased in sand at pH 9.
because of the similar zeta potential. The positive zeta potential of ZnO NPs at pH 5 and 7 and negative zeta potential at pH 9 have been reported by Kanel et al. [42]. These observations were true under all ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl2 (0.01, 0.05, and 0.1 mM)]. The breakthrough rates for all the transport experiment were observed at a pore volume of 2±0.5.

Column retention profile

Effect of ZnO NPs on the retention of TiO2 NPs. The retention profiles of TiO2 NPs and ZnO NPs under all ionic strength conditions, both for the individual and co-transport experiments, were studied to check if co-transport of TiO2 NPs and ZnO NPs would affect the distribution of nanoparticles retained in quartz sand. As anticipated from mass balance data, the retention profile obtained was the reverse of the BTC curves.

At pH 5, under all examined ionic strength conditions in the absence of ZnO NPs in suspensions, the retained concentration of TiO2 NPs in quartz sand decreased log-linearly with increase in distance. Retained concentrations of TiO2 NPs in quartz sand decreased non-exponentially with distance. However, the retention profile of TiO2 NPs in presence of ZnO NPs was similar to the profile acquired in the absence of ZnO NPs (Figs 7, 8 and 9). This study

Fig 7. Retention profile of TiO2 NPs at pH 5 (with and without ZnO NPs). Retention graph of TiO2 NPs in presence and absence of ZnO NPs sand. In suspensions at 0.1, 1, and 10 mM ionic strengths in NaCl solutions and 0.01, 0.05, and 0.1 mM CaCl2 solutions at pH 5. Replicate experiments were performed under all conditions (n ≥ 2). Similar retention profile was observed in both individual (TiO2 NPs) and co-transport experiment (TiO2 NPs and ZnO NPs).

doi:10.1371/journal.pone.0134796.g007

Fig 8. Retention profile of TiO2 NPs at pH 7 (with and without ZnO NPs). Retention graph of TiO2 NPs in presence and absence of ZnO NPs sand. In suspensions at 0.1, 1, and 10 mM ionic strengths in NaCl solutions and 0.01, 0.05, and 0.1 mM CaCl2 solutions at pH 7. Replicate experiments were performed under all conditions (n ≥ 2). There was increase in retention profile of TiO2 NPs in co-transport experiment (TiO2 NPs and ZnO NPs). In presence of ZnO NPs in suspension of TiO2 NPs showed increase in retention of TiO2 NPs in porous media.

doi:10.1371/journal.pone.0134796.g008
demonstrated that the copresence of ZnO NPs in suspensions did not affect the retention of TiO2 NPs in sand at pH 5.

At pH 7, the BTC plateau was decreasing with the increase in ionic strengths (NaCl and CaCl2). Figs 7, 8 and 9 shows that TiO2 NP retention was delegate to the solution ionic strength. Under all ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl2 (0.01, 0.05, and 0.1 mM)] at pH 7, the retention being detected near the column inlet was highest. Additionally, in the presence of ZnO NPs, the retained concentration of TiO2 NPs was higher relative to the concentration retained in the absence of ZnO NPs.

At pH 9 under all ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl2 (0.01, 0.05, and 0.1 mM)], the retention being detected near the column inlet was highest (Figs 7, 8 and 9). The retained concentration of TiO2 NPs were higher in comparison to retention observed in the absence of ZnO NPs. These results indicated that at pH 9 (unfriendly conditions), the copresence of ZnO NPs in suspensions increases the retention of TiO2 NPs in sand. A close inspection of retention profiles of TiO2 NPs in the presence of ZnO NPs in suspensions versus those in the absence of ZnO NPs displayed that under all ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl2 (0.01, 0.05, and 0.1 mM)], the retention profiles of TiO2 in the presence of ZnO NPs were lower to those without ZnO NPs in suspension.

The retention profiles were the inverse of the plateaus of BTCs, as expected from mass balance considerations (S4 and S5 Tables). Retention of TiO2 NPs in sand at pH 5 was more because of the presence of opposite charges on sand and TiO2 NPs. Previous reports also showed that retention of TiO2 NPs at pH 5 was higher because at this particular pH, the positively charged TiO2 NPs tend to attract the negatively charged sand [38]. Moreover, at pH 7 and 9 the retention of TiO2 NPs was less in sand due to presence of similar zeta potential in sand and TiO2 NPs. The negative charge of TiO2 NPs and sand at pH 7 have also been reported by Han et al. [35]. This observation was true under all ionic strength conditions [NaCl (0.1, 1, and 10 mM); CaCl2 (0.01, 0.05, and 0.1 mM)].

Effect of TiO2 NPs in the retention of ZnO NPs. The retention profiles of ZnO NPs in presence and absence of TiO2 NPs were evaluated under three different pH conditions, 5, 7, and 9, and a series of ionic strengths [NaCl (0.1, 1, and 10 mM) and CaCl2 (0.01, 0.05, and 0.1 mM)]. At pH 5, the BTC curves of ZnO NPs were very low due to the opposite charge present between sand and ZnO NPs. So, the retention profile of ZnO NPs in absence of TiO2 NPs was very high as shown in Figs 10, 11 and 12. The retention profile of ZnO NPs in the presence of TiO2 NPs was higher in sand.
At pH 7, the concentrations of ZnO NPs retained in sand alone were more than that of ZnO NPs copresent with TiO$_2$ NPs in the suspensions (Figs 10, 11 and 12). These observations showed that the copresence of TiO$_2$ NPs in suspension decreased the deposition of ZnO NPs in sand under all examined conditions. A close comparison of the retention profiles of ZnO NPs in the presence of TiO$_2$ NPs versus those in the absence of TiO$_2$ NPs showed that under all examined conditions, the decreased retention of ZnO NPs induced by the copresence of TiO$_2$ NPs in the suspension occurred across the entire column. Moreover, the shapes of the retention profiles of ZnO NPs in the presence of TiO$_2$ NPs were similar to those in the absence of TiO$_2$ NPs in suspensions.

In addition, under the examined pH 9, the concentrations of ZnO NPs retained in sand alone were more than that of ZnO NPs copresent with TiO$_2$ NPs in the suspensions (Figs 10, 11 and 12). The observation showed that the copresence of TiO$_2$ NPs in suspension decreased the deposition of ZnO NPs in sand under all examined conditions. A close comparison of the retention profiles of ZnO NPs in the presence of TiO$_2$ NPs versus those in the absence of TiO$_2$ NPs showed that under all examined conditions, the decreased retention of ZnO NPs induced by the copresence of TiO$_2$ NPs in suspension occurred across the entire column. Moreover, the shapes of the retention profiles of ZnO NPs in the presence of TiO$_2$ NPs were similar to those in the absence of TiO$_2$ NPs in suspensions.

The retention profiles were the inverse of the plateaus of BTCs, as expected from the mass balance considerations (S6 and S7 Tables). The retention of ZnO NPs was more in sand (Figs 10 and 11) due to opposite charges on ZnO NPs and sand at pH 5 and 7. Moreover, at pH 9,
the retention of ZnO NPs was less in sand, because both sand and ZnO NPs acquire negative charges (Fig 12). Previously stated reports also showed that the zeta potential of ZnO NPs vary with pH i.e. at pH 5 and 7, the zeta potential was positive, and at pH 9, it was negative [42].

Characterization of transport and transported material

Transmission electron microscopy (TEM). The size and shape of both TiO$_2$ and ZnO NPs, in presence of 10 mM of NaCl, before and after transport through porous media were examined by transmission electron microscopy (TEM) at three different pH of about 5, 7, and 9. 10 mM of NaCl was chosen based on the high ionic strength. The TEM image of TiO$_2$ NPs before transport through porous media shows the uniform distribution of NPs with average sizes of 350, 345, and 363 nm at pH 5, 7, and 9, respectively (Fig 13A, 13C and 13E). The morphology of TiO$_2$ NPs was observed to be spherical. Further, the average particle sizes of TiO$_2$ NPs at pH 5, 7, and 9 after transport through porous media were noted to be 642, 550, and 489 nm (Fig 13B, 13D and 13F). The sizes of ZnO NPs at pH 5, 7, and 9 were found to be 310, 335, and 333 nm before transport through porous media, and the sizes were 513, 550, and 489 nm after transport through porous media (Fig 14A, 14C and 14E).

![Fig 13. Transmission electron micrograph of TiO$_2$ NPs. A- Transmission electron microscopic image of TiO$_2$ NPs before transport at pH 5. B- Transmission electron microscopic image of TiO$_2$ NPs after transport at pH 5. C- Transmission electron microscopic image of TiO$_2$ NPs before transport at pH 7. D- Transmission electron microscopic image of TiO$_2$ NPs after transport at pH 7. E- Transmission electron microscopic image of TiO$_2$ NPs before transport at pH 9. F- Transmission electron microscopic image of TiO$_2$ NPs after transport at pH 9.](image-url)
The TEM image of ZnO NPs shows the uniform distribution of spherical-shaped NPs (Fig 14A–14F).

The increase in the size of TiO2 and ZnO NPs after transport was due to the agglomeration of nanoparticles. The differences in particle size of TiO2 and ZnO NPs for the tested pH 5, 7, and 9 were found to be insignificant before transport through porous media. The particle sizes of both NPs determined by TEM analysis were found to be in correlation with the DLS results. Even though the particles were found to be agglomerated after transport through the porous media, the morphology of NPs remained unchanged.

X-ray diffraction analysis. X-ray diffraction analysis was carried out to identify the crystal phases and to determine the crystalline size of material. The XRD pattern of TiO2 NPs (S1 Fig) shows the diffraction peaks at 25.2°, 37.81°, 47.9°, 54.0°, 54.9°, 62.6°, 68.8°, 70.3°, 75.2°, and 82.7°, which corresponds to (101), (004), (200), (105), (211), (204), (116), (220), (215), and (303) crystal planes. All diffraction peaks are well defined and perfectly matched with JCPDS card file no. 21–1272, and this confirms the presence of anatase as a predominant phase. Similar, X-ray diffraction were reported by Sadiq et al., [43] and Wei et al., [44]. The crystalline size of TiO2 NPs calculated from XRD patterns was 13.8 nm. Further, the X-ray diffraction analysis of ZnO NPs (S2 Fig) showed ten diffraction peaks at 31.7°, 34.3°, 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, 69.0°, and 72.5°, assigned to (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) crystal planes. This result reveals the characteristic hexagonal wurtzite structure of ZnO NPs when compared with the card file no. 5–0664 of the JCPDS database [45]. The crystalline size of ZnO NPs calculated from XRD patterns was 53.09 nm.

Similarly, the X-ray diffraction analysis of TiO2 and ZnO NPs in presence of sand was also performed to observe the phase change of NPs. The XRD pattern of TiO2 and ZnO NPs in presence of sand shows the diffraction peak of TiO2 and ZnO NPs combined with the characteristic peaks of silica (at 20.9°), whereas, no overlapping of diffraction lines was observed between the two analytes. Thus, these results indicated that the crystalline shape of NPs was retained in the presence of sand (S3 and S4 Figs). The crystalline sizes of TiO2 NPs and ZnO NPs calculated from XRD patterns in presence of sand were 96.53 and 78.91 nm.

Fourier transform infrared spectroscopy. The FTIR analysis of TiO2 NPs were carried out and the data were compared to understand their behavior before and after transport through sand. The secondary derivative spectra of TiO2 NPs at pH 5 before transport (control) showed the presence of a sharp peak at 412 cm⁻¹, corresponding to the stretching vibration of Ti–O–Ti [46]. The secondary derivative spectra of TiO2 NPs at pH 7 and 9 before transport
also showed the presence of Ti–O–Ti stretching vibration peaks at 410 and 412 cm\(^{-1}\), as expected for TiO\(_2\) NPs. In contrast to the TiO\(_2\) NP spectrum before transport, the absence of Ti–O–Ti peak was observed in the spectra of TiO\(_2\) NPs after transport (at pH 5, 7, and 9), which indicates the absence/less release of TiO\(_2\) NPs as compared to the control (S5 Fig).

Similarly, the FTIR spectra was also recorded for ZnO NPs before and after transport at pH 5, 7, and 9. The secondary derivative spectra of ZnO NPs before transport (control) shows a significant peak around 417 cm\(^{-1}\) at pH 5 and 408 cm\(^{-1}\) at pH 7 and 9 that can be assigned to the vibration mode of Zn–O bonding [47, 48]. The presence of Zn–O bond at 417 cm\(^{-1}\) recorded for ZnO NPs after transport (at pH 5, 7, and 9) indicates the release of ZnO NPs (S6 Fig).

**Conductivity Measurement.** For both TiO\(_2\) NPs and ZnO NPs, the conductivity was found to increase with increase in ionic strength under all pH conditions (5, 7, and 9) (S8 and S9 Tables). However, in the case of ZnO NPs, the conductivity was more than TiO\(_2\) NPs. The conductivity was almost similar before and after TiO\(_2\) NP and ZnO NP transport in sand column.

**Conclusion**

The current study suggests that the cotransport of TiO\(_2\) NPs and ZnO NPs in water-saturated porous media is much more complex than the transport of single nanoparticles. It also gives us a better understanding on the importance of cotransport of multicomponent nanoparticles as well as transport of individual nanoparticles in real aquatic environments, which are more complicated than those simulated in our study. Therefore, to better understand the cotransport behavior of TiO\(_2\) and ZnO NPs nanoparticles, further research is required to incorporate the effect of other factors (e.g., nanoparticle concentration and natural organic matter), which could influence the stability and interaction of nanoparticles.

**Supporting Information**

S1 Fig. XRD pattern of procured TiO\(_2\) nanoparticles. (TIF)

S2 Fig. XRD pattern of procured ZnO nanoparticles. (TIF)

S3 Fig. XRD pattern of procured TiO\(_2\) nanoparticles and sand. (TIF)

S4 Fig. XRD pattern of procured ZnO nanoparticles and sand. (TIF)

S5 Fig. FTIR spectra of TiO\(_2\) NPs before and after transport through sand at pH 5, 7 and 9. (JPG)

S6 Fig. FTIR spectra of ZnO NPs before and after transport through sand at pH 5, 7 and 9. (TIF)

S1 Table. Mean hydrodynamic size and zeta potential values of TiO\(_2\) NPs at different ionic strengths NaCl (0.1, 1, 10mM) and CaCl\(_2\) (0.1, 1, 10mM) and pH 5, 7 and 9. (DOCX)

S2 Table. Mean hydrodynamic size and zeta potential values of ZnO NPs at different ionic strengths NaCl (0.1, 1, 10mM) and CaCl\(_2\) (0.1, 1, 10mM) and pH 5, 7 and 9. (DOCX)
S3 Table. Zeta Potential values of fine sand in presence of NaCl (0.1, 1, 10mM) and CaCl₂ (0.01, 0.05, 0.1mM) at pH 5, 7 and 9.

S4 Table. Mass Balance of TiO₂ NPs in different pH (5, 7 and 9mM) and ionic strengths (NaCl-0.1, 1, 10mM) conditions.

S5 Table. Mass Balance of TiO₂ NPs in different pH (5, 7 and 9) and ionic strengths CaCl₂(0.01, 0.05, 0.1mM) conditions.

S6 Table. Mass Balance of ZnO NPs in different pH (5, 7 and 9) and ionic strength (NaCl-0.1, 1, 10) conditions.

S7 Table. Mass Balance of ZnO NPs in different pH (5, 7 and 9) and ionic strength CaCl₂ (0.01, 0.05, 0.1) conditions.

S8 Table. Conductivity of TiO₂ NPs solution at different pH (5, 7 and 9) and ionic strengths (NaCl-0.1, 1, 10; CaCl₂-0.01, 0.05, 0.1).

S9 Table. Conductivity of ZnO NPs solution at different pH (5, 7 and 9) and ionic strength (NaCl-0.1, 1, 10; CaCl₂-0.01, 0.05, 0.1).

Acknowledgments
We would like to thank VIT University, Vellore, India for giving the work space to carry out the research and X-ray diffraction facility at SAS, VIT University, Vellore, India.

Author Contributions
Conceived and designed the experiments: JK RN A. Mukherjee. Performed the experiments: JK AR AV A. Mathur SS. Analyzed the data: JK AR SS MP NC RN A. Mukherjee. Contributed reagents/materials/analysis tools: NC A. Mukherjee. Wrote the paper: JK A. Mukherjee.

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