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Influence of Solution chemistry and Natural water system on the Co-Transport of Aluminum oxide Nanoparticles with Tetracycline in porous media

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ABSTARCT

The coexistence of pollutants present in the ecosystem can also affects the fate and transportation of aluminum oxide nanoparticles (Al_2O_3 NPs). This study investigates the co-transport of Al_2O_3 NPs in solution and saturated porous media in the presence of tetracycline (TC). The study examines the impact of nanoparticle concentration on mobility at various concentrations of Al_2O_3 NPs with under various solution chemistry and the aggregation rate was higher with increased ionic concentration. Compared to the other natural water the aggregation was greater in lake water. In column transportation, the impact of nanoparticle concentration on mobility was examined at different TC concentrations. The elution concentration of Al_2O_3 NPs increased with increased TC concentration. Al_2O_3 NPs showed greater mobility at pH 7 and 3 than at pH 5. The surface of NOM stabilized Al_2O_3 NPs was surface modified with different concentrations of humic acid, resulting in higher mobility of NPs. Lake water had high hardness and chloride ions, leading to greater transportation of nanoparticles. This is in contrast to sedimentation studies, greater particle settling was observed when lake water was present. The study's findings suggest that both adsorption and transport of aluminum oxide impacted by the presence of TC and other organic matters in the environment.

Keywords: Aluminum oxide nanoparticles, Tetracycline, Co-transportation,ionic strength, Natural organic matter, Natural water.

1.Introduction

The utmost prevalent element in the earth crust was aluminium and it acquires 3rd most elemental composition in lithospheres. There no evidence on the role of aluminium in the biochemical processes of the living organisms. As an active amphoteric metal, aluminum often develops a white oxide coating on its surface. The widely known forms of aluminum oxide are α-, β-, and γ-Al_2O_3(Brough and Jouhara, 2020).The distinctive features of nanosized aluminum oxide (α-and γ-Al_2O_3), including greater mechanical strength, a higharea-to-volume ratio, remarkable hardness, and superior chemical stability, have facilitated their increasing utilization across a wide range of applications(Załęska-Radziwiłł et al., 2020). It is specifically suggested that Al_2O_3NPs be used as adsorbents, additions into concrete mixes, tribological enhancers for lubricants, and primary materials for the production ceramic, in the textile and cosmetic manufacturing, and as catalyzers(Nogueira et al., 2020). The potential application of Al_2O_3NPs in biomedicine, particularly as an antibacterial agent, is highly intriguing; presently, there is a lack of information on the processes by which these nanoparticles inhibit microbial development(Hassanpour et al., 2018).

For several decades, tetracyclines (TCs) have been a widely utilized antibiotic in cattle feed and disease management because of their excellent therapeutic properties. These substances have found their way into the water and soil ecosystems as a result of the extensive use of TCs and other antibiotics(Chen et al., 2018). Continuouscontact to the antibiotics, either alone or in combination with other toxic pollutant mayput burden on the reducing the effectiveness and therapeutic value of antibiotics. And also on emergence of antibiotic-resistant bacteria, despite environmental antibiotic concentrations typically remaining below levels that directly impact bacterial populations and other vulnerable species (Amangelsin et al., 2023).

To effectively evaluate the dangers associated with antibiotic pollutants and create mitigation plans, it is essential to comprehend the fate of these pollutants in the soil-water ecosystem. For several decades, TCs have been a widely utilized antibiotic in cattle feed and disease management because of their excellent therapeutic properties(Ling et al., 2021). These substances have found their way into the water and soil ecosystems as a result of the extensive use of TCs and other antibiotics. Geographical conditions (such as those found in the humid tropics, where high temperatures and heavy rain are common) weathering or human activity will accelerate and raise the amount of aluminum oxide in soils. Trace organic pollutants, as TC antibiotics, can be prevented from spreading and migrating by adsorption on aluminum oxides(W. R. Chen and Huang, 2010).

The atom (Al (III))of aluminum oxides have an acid center and may accelerate the dehydration, oxidation, dimerization, and isomerizationof organic molecules in addition to adsorbing them(Pines and Haag, 1960). Alumina's inherent acidity and catalytic activity make it the most significant catalyst materials in industrial processes. The possible influence of Al_2O_3NPs surfaces on the conversion of tetracycline was not explored thoroughly, despite the well-known high adsorption of TCs to aluminum oxides(Zhang et al., 2010).

Aluminium oxide nanoparticles can adsorb and carry tetracycline, which is an antibiotic, through porous media such as soils and filtration systems. The co-transportation effect is affected by various environmental conditions, including pH, the amount of other ions, and flow rates through the medium(Chen et al., 2018). The pH can affect the charge and solubility of both the TC and the nanoparticles, which in turn can alter their interaction and mobility. Ionic strength (IS) refers to the concentration of other ions in the solution, which can contend with TC for binding sites on the nanoparticles or change the aggregation state of the nanoparticles. Flow rate impacts the nanoparticles and the antibioticsmovement through the media and can influence the extent of their interaction as well(W. R. Chen and Huang, 2010).

Studying the co-transportation actions of aluminium oxide nanoparticles and TC in porous material can provide valuable information on how to optimize filtration and purification systems to selectively remove contaminants like pharmaceuticals from water sources. However, it should be noted that while co-transportation can be beneficial for environmental applications, it also raises concerns about the fate and transport of nanoparticles in the environment, which need to be carefully considered(W.-R. Chen and Huang, 2010).

To investigate the co-transportation of Al_2O_3 NPs with TC in saturated porous medium, a series of experimental studies were performed. In our previous study, the characteristics of the nanoparticles were analyzed individually. Subsequently, a set of experiments were designed to study their combined transport behavior in porous media under varying environmental factors like pH, IS, and flow rates. Co-transportation of Al_2O_3NPs with tetracycline in porous media refers to the simultaneous movement of these two entities through a filterable substrate. This interaction is key to environmental science and engineering because it combines the use of nanoparticles with pharmaceutical compounds to potentially enhance remediation and water treatment processes. Understanding the co-transportation of Al_2O_3 NPs with tetracycline in porous media has significant implications for environmental remediation and water treatment strategies. The data acquired from this could aidfor the advanced and more effective approaches for contaminant removal and water purification in various environmental settings.

2. Materials and Methods

2.1. Suspension preparation

50 nm sized Al_2O_3 NPs (99.8% pure) were procured from Merck, India. To prepare the stock solution of nanoparticles, Al2O3 nano-powder was suspended in ultrapure water (100 mg/L concentration) and sonicated for 30 minutes with ultra-sonicator at 550W (Sonics, USA).
Tetracycline (TC) powder was procured from sigma Aldrich, India. To prepare the stock solution, 30 mg of TC was added to the 1 L milli-q and kept under stirring for 24hours and then filtered with 0.45umsize filter(Thiagarajan et al., 2022).

2.2. Characterization

Characterization of the Al_2O_3NPs in the presence of TC was done using FTIR, SEM, zeta potential and particle size analysis. Utilizing Bruker machinery and Cu K radiation (= 1.5418), the XRD pattern was produced. Examining the morphological, topographic, and particle size differences of Al_2O_3NPs during the interaction with TC was done using SEM (ZEISS(EV018)). The particle sizes and surface chargeof aprepared suspension of Al_2O_3 NPswith TC, were investigated using Zetasizer (Brookhaven Instruments Corporation, USA). Energy dispersive X-ray analysis (EDX) was performed to measure the elemental composition of materials(Farahmandjou and Golabiyan, 2016; kumar Chilakapati and Pulimi, 2023).

2.3. Aggregation of tetracycline on the Al_2O_3 NPs

2.3.1. Impact pH on aggregation of Al_2O_3 NPs in the combination with Tetracycline

The aggregates of the Al_2O_3 NP suspensions under various pH backgrounds could be described by measuring, the average particle size changes over time. The pH (3,5 and 7) range were modifiedwith 1N NaOH and HCl to attain the correct pH(kumar Chilakapati and Pulimi, 2023). After pH was adjusted, 50 mL TC stock and Al_2O_3NPs solution wasmixed in a beaker. 1 ml of sample containing $A1_2O_3$ (100 mg/L) and TC (30 mg/L) was taken every 15 minutes, and Zetasizer was used to analyse the particle size and its surface charge (Qi et al., 2018).

2.3.2. Effect of Ionic strength on aggregation of Al_2O_3 NPs in the presence of Tetracycline

Therate of aggregation and influence of ionic strengthon aggregation of $A1_2O_3$ NPs with TC suspension were measured at varying NaCl concentration (10, 50 and 100mM of NaCl). For 90 minutes the tests were carried out in a glass beaker. The suspensions were then ultrasonically dispersed thoroughly to scatter the particle in the solution. Every 15minutes of interval 1ml of the sample was collected and particle size and zeta potential were measured using Zetasizer(Zhao et al., 2021).

2.3.3. Effect of Humic acid concentration on aggregation of Al_2O_3 NPs in the presence of Tetracycline

Aggregations of Al_2O_3 NPs with TC suspensions in various HA solutions (0.1,1 and 10ppm of humic acid) were characterized by monitoring changes in the average particle size and zetapotential over time. The overall experiment was conducted for 90minuteswith volume 50 ml of aqueous suspension containing Al_2O_3NPs (100mg/L) and TC (30 mg/L) was taken every 15 minutes once for size and charge measurement(Ling et al., 2021).

2.3.4. Effect of Particle concentration on aggregation of Al_2O_3 NPs with Tetracycline

Al_2O_3 NPs in the TC were taken at varied particle concentrations to determine the pace of aggregation and the impact of particle concentration (10, 50 and 100 ppm of Al_2O_3NPs). The experiments were conducted in a glass beaker for 90 minutes. The different particle concentrations of 10, 50, and 100 ppm of Al_2O_3NPs suspension with TC, were taken in a beaker. After that, the suspensions were extensively ultrasonically dispersed throughout the liquid. 1ml of the sample was taken every 15 minutes, and Zetasizer was utilized to quantify the particle size and surface charge (Sadiq et al., 2011).

2.4. Co-transport of Al2O3 along with TC in different solution chemistry

The co-transportation studies were performed with sand packed Econo column (Bio-Rad Laboratories) with the depth of 50 mm. The columns were first pre-equilibrated with a background solution maintained at constant pH and IS and a minimum pore capacity of 10. After pre-equilibration, four pore volumes (PV) of NPs and TC suspension, ten PV of NaCl with the similar IS, humic acid (HA), and pH, and five pore volumes of Milli-Q water were added to the column(Solovitch et al., 2010). Using a peristaltic pump (Mic—Lins pp-30EX) the solutions were introduced into the columns using a downward flow.

To prevent NPs settling and maintain suspension stability at the chosen suspension chemistry, NPs and TC suspension are periodically sonicated during column studies. The transport tests were completed using different pH (3,5,and 7), HA (0.1,1 and 10ppm)and three varied ionic strengths (10,50 and 100mM NaCl). UV-Spec (Jenway) was used to measure the collected samples at 360 nm. To ensure accurate depiction of fluid velocities within the coarse aquifer sediments, the flow rate for all tests was adjusted at 1 mL/min (Lu et al., 2021). UV-Spec (Jenway) was used to measure the collected samples at 360 nm(Kumari et al., 2016).

3. Results and Discussion

3.1. Characterization of Al_2O_3 NPs with TC

Using FTIR and FESEM, the chemical structures and morphologies of Al_2O_3 NPs as well as the modifications to Al_2O_3NP's morphology and chemical structure when combined with TC were investigated.Stretching O-H (aluminum hydroxide) and AlO_4 bonds are represented by the peaks at 3317, 2367.4, 2104.7, and 1629.54 cm-1 in the FTIR patterns of Al_2O_3 NPs and Al_2O_3 when combined with tetracycline (Alamouti et al., 2021; Nila, 2018). Peaks from 3317 to 3308.6 cm^{-1}, 2367.4 to 2362.09 cm^{-1}, 2104.7 to 2113.08 cm^{-1}, and 1629.54 to 1637.91 cm^{-1} were shifted as a result of TC binding (Figure 1.).

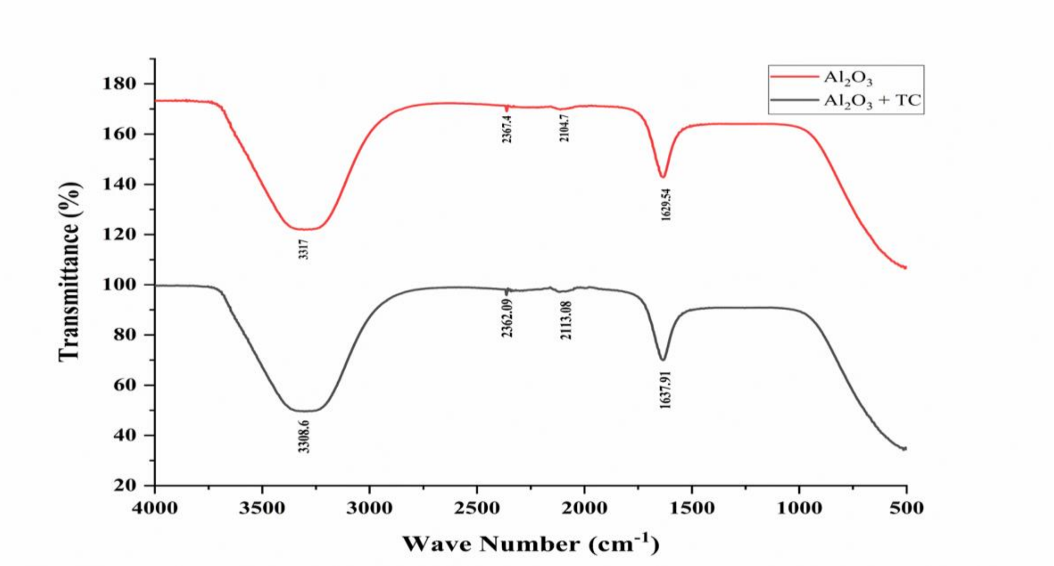

Figure 1.FTIR pattern of Al_2O_3 NPs (100ppm), Al_2O_3 NPs (100ppm) with TC (30ppm)

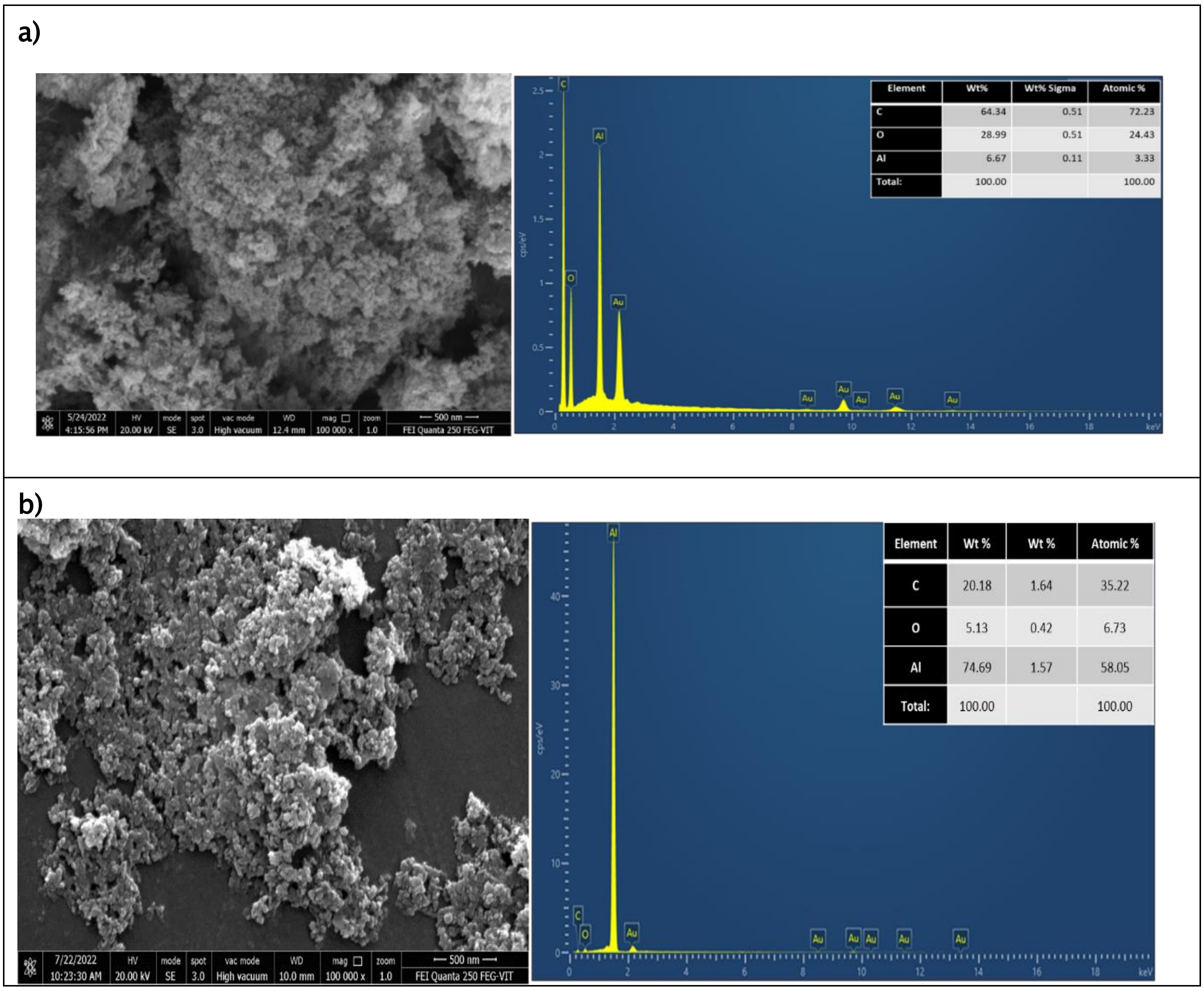

Figure 2. FE-SEM and EDAX pattern image of Al_2O_3 NPs (100ppm) with TC (30ppm)

Nano Al_2O_3 particles with spherical and cubic forms and sizes less than 25 nm are shown in Figure 2. The aggregation of nano Al_2O_3 NPs with TC is seen in Figure 2. The aggregation of Al_2O_3 with TC was found to be greater than that of Al_2O_3 NPs alone, owing to the binding of TC to the surface of Al_2O_3 (Figure 2Aand 2B). Dynamic light scattering analysis was used to confirm the aggregation further. The surface binding of TC to the surface of Al_2O_3 NPs is verified by the EDAX pattern(Prashanth et al., 2015).

To evaluate the stability of the particles, the effective diameter of Al_2O_3 NPs in suspension was measured both with and without TC. As can be seen from table 1, the results showed that the effective diameter of Al_2O_3 NPs increased when TC was present. Al_2O_3NPsaggregates differently when the particle size increases. The aggregation pattern Al_2O_3 with TC was studied with varying ionic strength, pH, natural organic matter (HA) and also in different natural water system(W.-R. Chen and Huang, 2010).

3.2. Aggregation of tetracycline on the Al_2O_3 NPs

3.2.1 Effect of pH on aggregation of Al_2O_3 NPs with Tetracycline

The impact of pH on the aggregation of Al_2O_3NPs with tetracycline was investigated under various pH (3,5 and 7). Figure 3 demonstrates the alteration in the particle size of Al_2O_3nanoparticlesin the presence of TC molecules at different pH levels.The Al_2O_3 nanoparticles exhibit stability at pH 7, with a measured particle size of 278.4 nm. The particle size was increased due to the adsorption of TC on to its surface. At pH 5 the size of the Al_2O_3 NPs was increased to 460.7 nm at 30minutes of TC adsorption.Numerous ionizable functional groups, including as dimethylamine, phenolic diketone groups and tricarbonyl methane are present on TC molecules of various veterinary antibiotics. It was discovered that the dimethylamine groups on TC molecules were protonated as a result of the TC adsorption that occurred alongside the H+ adsorption. When comparing pH 5 to pH 3 and pH 7, the rate of settling was greater. According to the aforementioned findings, TC molecules alter the nature of Al_2O_3 NPs by enhancing the particle size at various pH values(Babakhani et al., 2017; Qi et al., 2018).

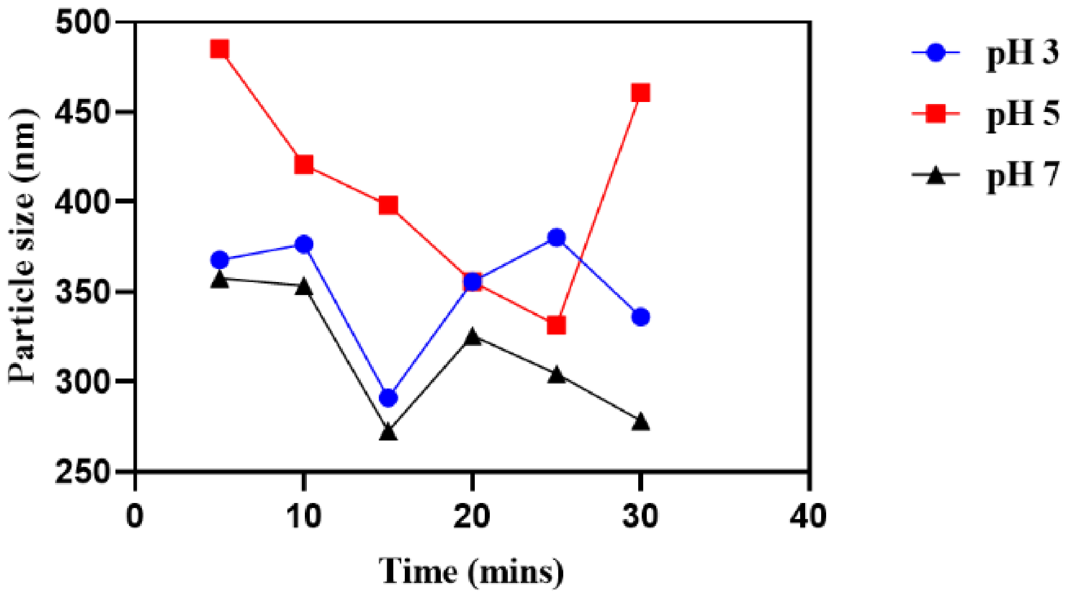

Figure 3. Aggregation of Al_2O_3 NPs (100ppm) along with TC (30ppm) in different concentration pH

3.2.2. Impact of Ionic strength on aggregation of Al_2O_3 NPs with Tetracycline

The Al_2O_3NPs aggregation is altered by TC molecules under varying ionic strengths. Figure 4 showed the aggregation pattern of Al_2O_3NPs at different NaCl concentration. Enhancement in the NaCl concentration providing a faster aggregation of Al_2O_3 NPs. In the presence of TC at higher NaCl concentration the size of the Al_2O_3 NPs was elevated from 296.5 to 1705.9 nm. Regarding the IS in destabilizing Al_2O_3 NPs, two major conclusions may be made. First, the surface charge of Al_2O_3 NPs may be lowered by the IS. Secondly, the double layer is compressed by the ionic strength, resulting in a decrease in the double-layer's thickness and a reduction in the repulsive electrostatic interactions among the NPs (Thio et al., 2011). Similar but more precise predictions are made by the more contemporary. According to Fig. 4, when the concentration of salt increased, the zeta potentials of Al_2O_3 NPs dropped. Nevertheless, at the greater Cl^-concentrations, the NPs accumulated. We suggest that the double layer's compression was the cause of the NP aggregation driven on by Cl. Based on the results mentioned above, we suggest that the stronger electrostatic repulsion interactionsamong the NPs and TC molecules improved the stability of Al_2O_3 NPs due to the presence of TC molecules. Since TC molecules have a molecular weight of 444 g/mol, it's possible that the TC adsorbed layer's thickness is insufficient to Al_2O_3 NPs over the Van der Waals attraction range. Though, the primary reason for NP aggregation induced by Cl^- was the reduction of the double layer (W.-R. Chen and Huang, 2010; Qi et al., 2018).

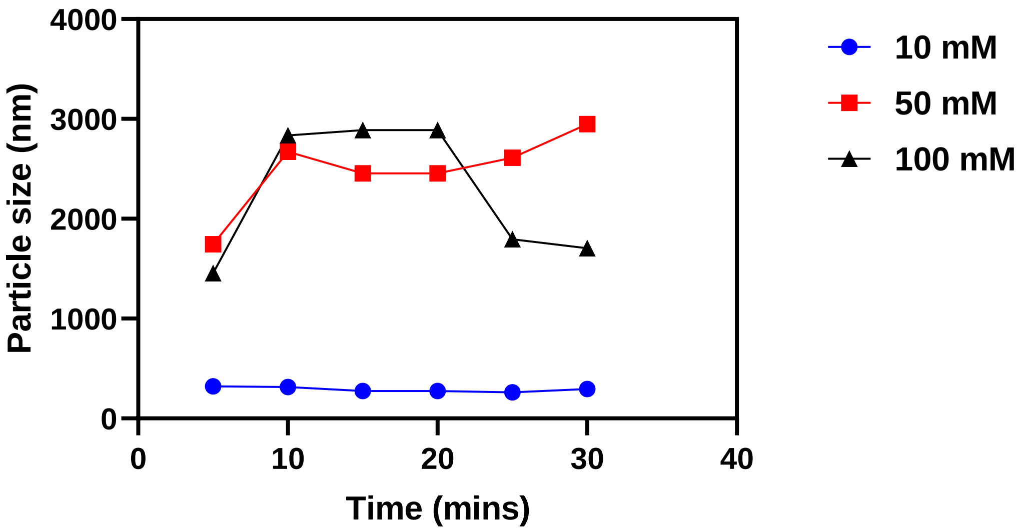

Figure 4. Aggregation of Al_2O_3 NPs (100ppm) along with TC (30ppm) in different concentration of IS

3.2.3. Effect of HA concentration on aggregation of Al_2O_3 NPs with Tetracycline

Figure illustrates how TC molecules affect the Al_2O_3 NPs aggregation behavior at various HA solution concentrations. The Al_2O_3 NPs stabilized as the concentration of HA increased. The Al_2O_3 NPs size of the particles was maintained at around 360.67 nm. The aggregation behavior of Al_2O_3 NPs was altered upon adsorption of TC molecules onto their surfaces. Figure 5 demonstrates that the Al_2O_3 NPs started to aggregate as the concentration of HA decreased. As the HA concentration reached 0.1 ppm, particle size of the Al_2O_3 NPs rose to 392.6 nm. But when the HA concentration increased more, the Al_2O_3 NPs aggregation slowed down.The surface variations of the Al_2O_3 NPs were mitigated when HA was adsorbed on particles mediated condensation, hydrogen bonding, electrostatic attraction, and Ti-O bonding(Liu et al., 2008). In the meanwhile, the ionization of the HA carboxylic group altered the zeta potential of the Al_2O_3 NPs (Sun and Lee, 2012). It was established that the TC molecules could either form hydrogen bonds or interact via electrostatic attraction with the free humic acid in the solution, or they could form surface complexations and cation exchanges with minerals leads to the aggregation of Al_2O_3 NPs at lower concentrations(ZHAO et al., 2012).

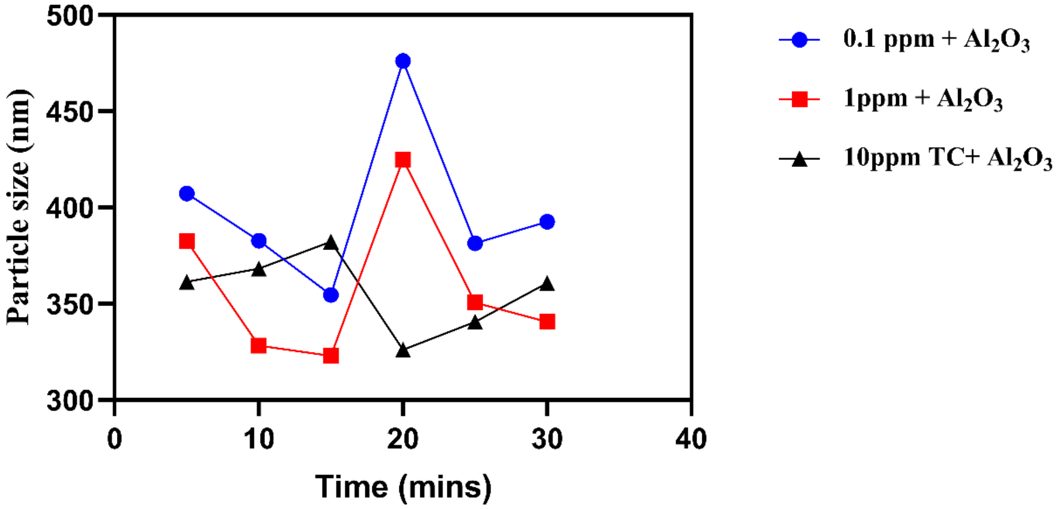

Figure 5. Aggregation of Al_2O_3 NPs (100ppm) along with TC (30ppm) in different concentration of NOM condition

3.2.4. Effect of Particle concentration on aggregation of Al_2O_3 NPs with Tetracycline

The settling pattern of the Al_2O_3 NPs at various concentration of TCis depicted in Fig. 6. The particle size of Al_2O_3 NPs reducedto 292.5 nm with an elevated TC concentration after the various TC concentration were adjusted in solution (Figure 1b). It was noted that the absorption of H+ ions coincided with the adsorption of TC, resulting dimethylamine group protonation on TC molecules(Li et al., 2010). The electrostatic repulsion forces among the particlesstrengthened due to the increased particle size. Moreover, the NPs became more stable due to the rise in electrostatic repulsion forces(Chen et al., 2018). Apart from the impact of sedimentation with big particles, there was a minor disaggregation of the NPs due to an increase in electrostatic repulsion forces. Nevertheless, the size of Al_2O_3 NPs was notreduced proportionally with the increase in TC concentration.At low TC concentrations, it was discovered that the enhanced electrostatic repulsion forces were insufficient to separate the Al_2O_3 NPs. To investigate the TC-induced aggregation of Al_2O_3 NPs under different circumstances, we selected a concentration of 10 mg/L(W.-R. Chen and Huang, 2010).

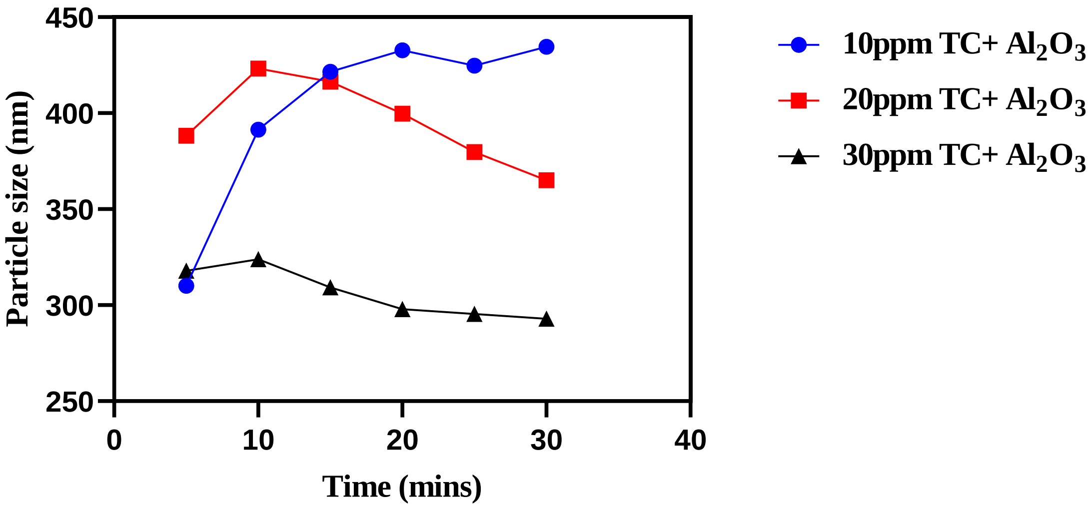

Figure6. Aggregation of Al_2O_3 NPs (100ppm) along with different concentration of TC

3.2.5. Effect of different natural water systems on aggregation of Al_2O_3 NPs in the presence of Tetracycline:

The particle size of Al_2O_3 NPs was higher (i.e. 13382.6 nm) in lake water was greater than in other natural water, resulted in greater particle aggregation Figure 7. The nanoparticles may absorb and complicate the organic materials, nutrients, heavy metals, and other substances found in the water, forming aggregates. The harder water causes the Al_2O_3 NPs in the presence of TC to settle out more quickly. The NPs' settling may also be accelerated by the lake water's chloride and calcium substances, which alter the electrostatic repulsion and energy barriers(Liu et al., 2018). Greater settling rates were found in natural waters with greater ionic concentrations and hardness(Chen et al., 2018; Thiagarajan et al., 2022).

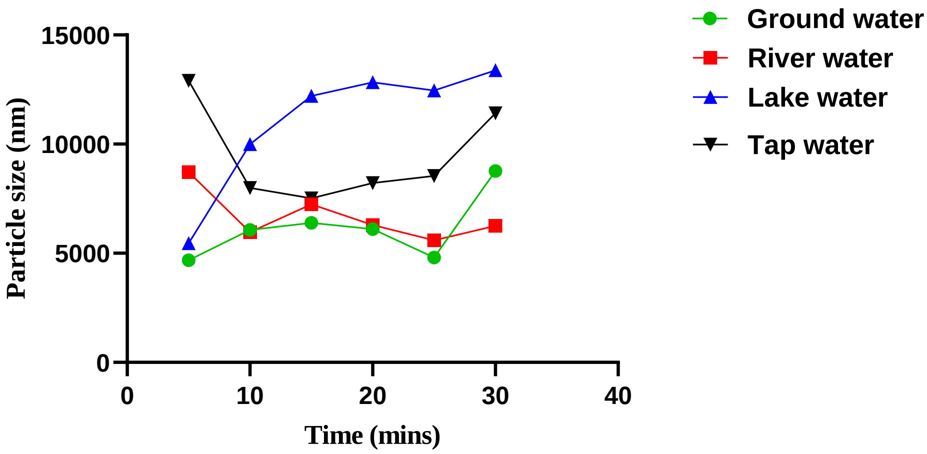

Figure 7. Aggregation of Al2O3 NPs (100ppm) along with TC (30ppm) in different natural waters

3.3 Co-transport of Al_2O_3NPs along with TC in different solution chemistry

3.3.1 Co-transport of Al_2O_3 NPs and tetracycline with varying Al_2O_3 NPs concentration

The effects of varying Al_2O_3 NPs nanoparticle concentrations on tetracycline fate and transport are shown in Figure8. According to this study, Al_2O_3 NPs nanoparticles transport was affected by tetracycline.Al_2O_3 NPs with TC, for instance, showed a high breakthrough (C/C0) of 0.0078 at PV of 6 in the presence of 10 ppm of Al_2O_3 NPs. TC strong adsorption capacity on the Al_2O_3 NPs surface was the reason for this result (Figure 8).

Al_2O_3 NPs and TC was retained on the quartz sand surface caused combat over the deposition sites, which in turn promoted the retention of AL2O3 NPS nanoparticles (Fang et al., 2017).

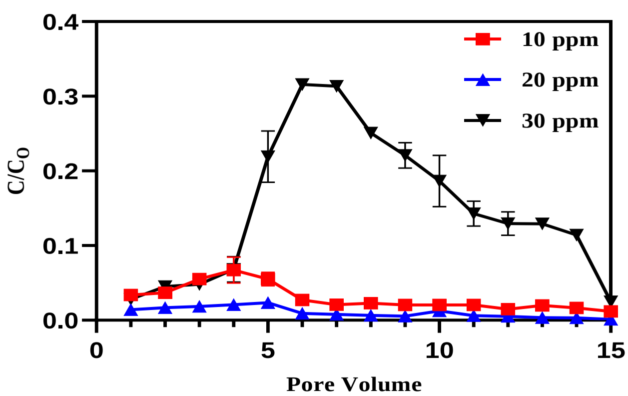

Figure 8. Breakthrough curves of Al_2O_3NPs (100ppm)with TC at different Concentration of TC (10 ppm, 20 ppm, and 30 ppm)

This finding indicates that the increase in TC there was decrease in transport of Al_2O_3 NPs. This outcome might have two possible causes. One the one hand, the mass of TC in the influent for the co-transport column studies was split equally between the aqueous solution and the solid phase, or clay colloids. At higher TCconcentrations (i.e., 30 ppm) than at lower TCconcentrations (10 ppm), the proportion of TC adsorbed onto Al_2O_3 NPs in the influent was higher. As a result, more Al_2O_3 NPs - tetracycline associated with the effluent could pass through the sand columns when the influent contained lower concentrations of TC.

It was found that one key reason for the enhanced transport of Al_2O_3 NPs by lower concentration of TC resulted in the increased in electrostatic repulsion between Al_2O_3 NPs nanoparticles and sand grains. More significantly, when the suspension passed through the column, with higher concentration of TC (30ppm) and Al_2O_3 NPs co-deposited on the sand surface (Fang et al., 2017; Qi et al., 2018). Lesse level TC thereby increased the mobility of nanoparticles and fought with Al_2O_3 NPs nanoparticles employed for deposition on quartz sand.

3.3.2 Co-transport of Al_2O_3 NPs and tetracycline at different pH conditions

The influence of pH (3,5 and 7) on the co-transport of Al_2O_3 NPs and tetracycline was studied since tetracycline antibiotics exhibited various species at different pH and the surface potential of Al_2O_3 NPs would change with the value of pH (Li et al., 2019). Under pH 5, TC were shown to behave as a carrier of Al_2O_3 NPs nanoparticles and improve its transportation in porous sand columns (Figure9).Remarkably, acidic circumstances, transport boosting impact of Al_2O_3 NPS was higher than in neutral environments. Al_2O_3 NPs have greater mobility at pH 7 and 3 than at pH 5.The breakthrough C/Co of 0.0143 reached 6 PV for pH 3 and 0.0072 at 6 PV for pH 5. For pH 7 breakthrough was around 0.014 at 6 PV. The outcome was associated with the varying affinities of tetracycline binding to Al_2O_3 NPS nanoparticles under varying pH circumstances(Zhang et al., 2019).

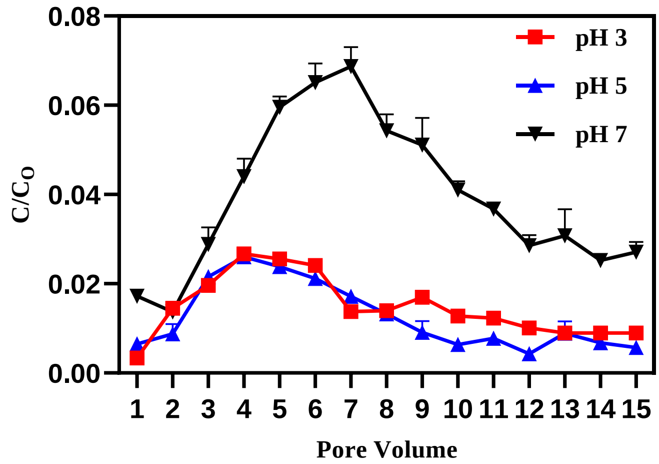

Figure 9. Breakthrough curves of Al_2O_3 (100ppm) with TC (30ppm) at different (A) pH (3,5, and 7)

The Al_2O_3 NPs surface properties, including surface charge and the deprotonation-protonation of its functional groups, were markedly influenced by the pH change from 3 to 7. Raising pH promotes deprotonation of a number of groups, including the COOH (carboxyl) group of Al_2O_3 NPs enol and amino groups of TC(Li et al., 2019; Zhang et al., 2011). Due to electrostatic repulsionsamong the carboxylic groups of Al_2O_3 NPs and the deprotonated amino/enol groups of the antibiotics, TC and Al_2O_3 NPs interact less well. Consequently, less tetracycline was adsorbed on Al_2O_3 NPs as the pH rose from 5.0 to 7, which reduced the nanoparticles' ability to mobilize pollutants.

3.3.3 Co-transport of Al_2O_3 NPs with TC under variedIS conditions

Raising the IS can significantly change the pattern of Al_2O_3 NPs aggregate (Qi et al., 2018; Zhou et al., 2016). This could have an impact on tetracycline's adsorption qualities (Ghosh et al., 2022; Guo et al., 2018) and therefore the co-transport of Al_2O_3 NPs and tetracycline in saturated porous sand media. The findings of an investigation into the impact of IS (varying NaCl concentrations) on the co-transport of Al_2O_3 NPs with TC are displayed in Figure 10. At higher ionic strength blocking was higher than lower ionic strength blocking, resulting in a lesser effluent plateau concentration for higher IS. For 50 mM NaCl, nanoparticle elution reached break-through at a C/C0 of 0.129 whereas for 10 mM NaCl at a maximum C/C0 of 0.125 and 100 mM NaCl at a maximum C/C0 of 0.078 with PV of 6 respectively. Due to the reduced electrostatic attraction between the deprotonated COOH groups of Al_2O_3 NPs and the dimethyl amino groups (positively charged) of TC, increasing the concentration of NaCl inhibited the binding of TC to Al_2O_3 NPs (Guo et al., 2018; Ling et al., 2021). In the meantime, the cationic bond was greatly deteriorated by the high NaCl concentration's electrostatic screening action, which decreased the surface charge.

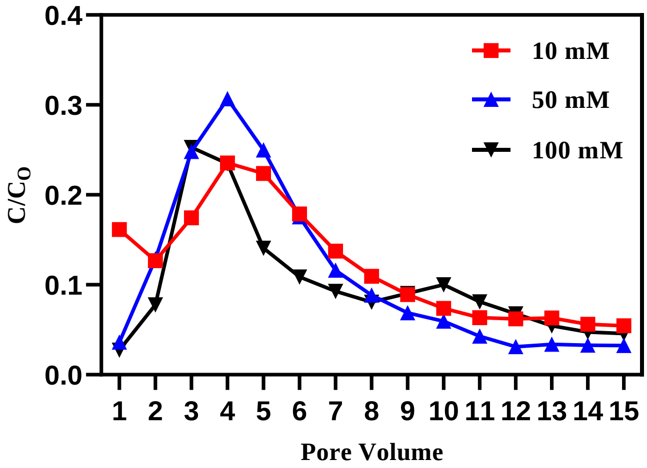

Figure 10. Breakthrough curves of Al_2O_3 (100ppm) with TC (30ppm) at different ionic strength (10mM, 50mM and 100mM)

Increasing ionic strength, on the other hand, greatly improved Al_2O_3 NPs flakes' ability to stack, which decreased the transport of Al_2O_3 NPs (Qi et al., 2018; Zhao et al., 2021). In this instance, there was less Al_2O_3 NPs -adsorbed TC transport across sand columns; as a result, Al_2O_3 NPs nanoparticles were better in mobilizing contaminants at 10 mM NaCl than they were at 100 mM NaCl. This finding clearly showed that the Al_2O_3 NPs nanoparticles' aggregation states were crucial to their capacity to mobilize contaminants (Liu et al., 2008).It was discovered that the influent's dissolved tetracycline transport was only marginally impacted by ionic strength (Figure 10.). Since tetracycline competitively impacted the deposition sites of Al_2O_3 NPs equally across three variedIS during the transport process, there were no discernible differences in how tetracycline affected the transport of Al_2O_3 NPs at varying IS.

3.3.4. Co-transport of Al_2O_3 NPs with TC under different NOM conditions

The Figure 11 shows the impact of presence of NOM on the co-transportation of Al_2O_3 NPs and TC in porous medium. The NOM stabilized Al_2O_3 NPs surface modified with different concentrations of humic acid by imparting a significant negative surface charge which in turn resulted in the higher mobility of Al_2O_3 NPs because of electrostatic stabilization betweenthe negatively charged collector and the nanoparticles(Qi et al., 2018).

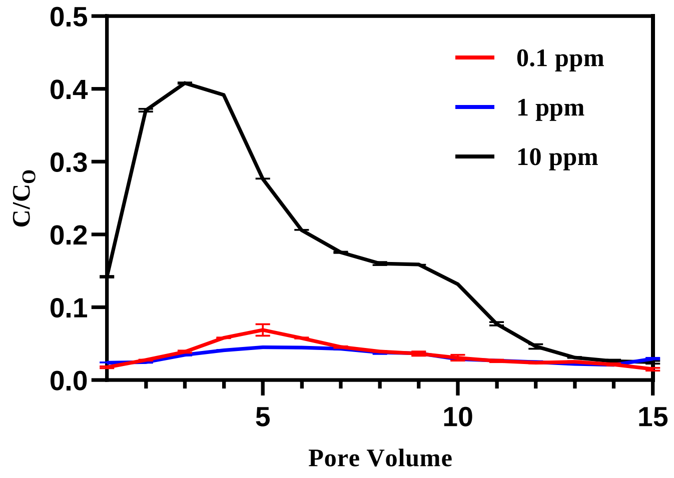

Figure 11. Breakthrough curves of Al_2O_3NPs(100ppm) with TC (30ppm) at different Concentration of Humic acid (0.1ppm, 1ppm, and 10ppm).

This was demonstrated by enhanced transport, which resulted in C/Co ratios, 0.028 with 6PV at 0.1ppm of HA, 0.024 with 6PV at 1 ppm and 0.37 with 6PV for 10 ppm. NOM progresses steric hindrance and electrostatic repulsion, enhancing the stability of the suspension and inhibiting the aggregation. NOM concentrations utilized for surface modification may have increased Al_2O_3 NPs transport by inhibiting strong adsorption sites on collector grain(Zhang et al., 2019).

3.3.5 Co-transport of Al_2O_3 NPs with TC under different natural water system

The impact of several natural water sources on the co-transportation of TC and Al_2O_3 NPs in the saturated porous media is depicted in the Figure 12.The concentration of Al_2O_3 NPs in the effluent notably declined in groundwater, tap and river water.

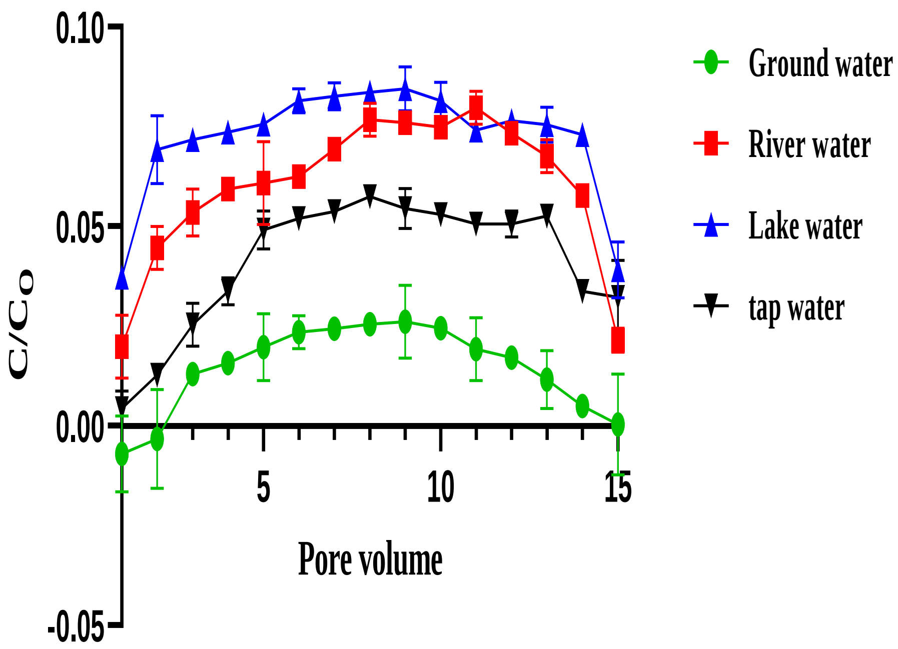

Figure 12. Breakthrough curves of Al_2O_3NPs(100ppm) with TC (30ppm) at different natural waters.

In the natural water system particles resulted in C/Co ratios approaching 0.0128 with 6PV for tap water, 0.0186 with 6PV for groundwater, 0.019 with 6PV for river water, and 0.0384 with 6PV for lake water. The lake water has a high level of hardness and chloride ions, and there has been an increase in the movement of NPs. This contrasts with the sedimentation trials, when the addition of lake water led to an increase in the aggregation of Al_2O_3 NPs(Yang et al., 2019).

4. Conclusion

In summary, the characteristics of NPs, porous media, and fluids alone or in combination through various mechanisms have a substantial influence on the Co-transport processes of Al_2O_3 NPs with TC in porous media. The most important characteristics among them are the fluids' size, surface coatings, NPs input concentration, particle size, pH, NOM, and IS. Furthermore, through the processes of adsorption, complexation, competition, and steric repulsion, NPs can change the way that coexisting contaminants are transported in porous surfaces. The modified physicochemical and hydrodynamic characteristics of the fluids may further interfere with this important carrier impact of NPs.The transport of NPs in porous medium may be impacted by interactions among the NPs and co-existing contaminants, which may potentially change the NPs' surface characteristics. Despite the impressive advancements in research on the fate and transport of Al_2O_3 NPs combined with TC in porous media, more studies are still essential due to the complex nature of these transport mechanisms. Few research has been done on the potential effects of hydrodynamic variables on the co-transport of contaminants and Al_2O_3 NPs in porous media, as well as the associated processes. It is important to continue researching the impact of hydrodynamic variables. The presence of other contaminants is probably going to have an impact on transportation Al_2O_3 NPs through porous medium. The way that Al_2O_3 NPs behave in the environment can also be changed by their interactions with other contaminants. Fewer research, particularly on co-existing NPs, have examined if co-existing contaminants can affect the movement of Al_2O_3 NPs. Further clarification of the interaction mechanisms and investigation of the impact of co-existing contaminants and other NPs apart from TC on the transport process of Al_2O_3 NPs in porous medium are necessary.

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