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# The use of silica encapsulated DNA particles with a supermagnetic iron core (SiDNAMag) in sand filtration system: Effect of water chemistry

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ABSTRACT

Sand filtration systems (SF) are a well-established approach in ensuring the availability of clean water. Understanding the transport properties of colloidal particles within SF systems is of paramount importance for optimizing their performance. This study investigated the potential utilization of silica-encapsulated DNA particles, equipped with a magnetic core to enhance particle separation and quantification efficiency (SiDNAMag). These particles were evaluated as tracers for delineating complex pathways and conducting source tracking within sand filtration (SF) systems for particulate substances. The study focused on exploring the sensitivity of SiDNAMag to solution chemistry, while elucidating the underlying mechanisms governing their transport and retention in sand filtration systems. Laboratory columns and HYDRUS-1D modeling were employed to analyze a range of water chemistry solutions, encompassing NaCl, $NaHCO_3$, $CaCl_2$, and $MgCl_2$, with ionic strengths ranging from 0.1 mM to 20 mM. The results revealed that the transport of DNA-tagged silica particles could be described by a first-order kinetic attachment and detachment rate coefficient. Elevated ionic strengths consistently led to increased particle adhesion and decreased rates of detachment. The sticking efficiencies of SiDNAMag particles exhibited a range of 0.7 to 1. The remarkable adhesive effectiveness can be ascribed to the comparatively low negative charge exhibited by SiDNAMag particles. This leads to the creation of unstable colloids and encourages the aggregation of these colloidal particles, thereby limiting the potential application of these particles as a tracer. In conclusion, this work underlines the potential of SiDNAMag particles as a potential subsurface tracer. However, further research is warranted to investigate strategies for reducing the interaction between these particles and sand, particularly in response to the chemistry of the infiltrated water.

## 1. Introduction

Sand filtration (SF) plays a pivotal role as a critical treatment stage in both natural and engineered water and wastewater treatment methodologies. With its broad application across various sectors and processes, this method offers a cost-effective and straightforward means of removing suspended matter, organic compounds, emerging contaminants, biological contaminants, and micro and nanoparticles from water sources [1,2]. Significantly, its adaptability goes beyond diminishing dependence on energy-intensive treatment procedures, offering supplementary advantages like cost-efficient operation, suitability for diverse scales of implementation, and the potential for seamless integration with complementary treatment methods to achieve specific water quality goals [3]. In efforts to optimize the performance of SF systems and comprehensively monitor water and contaminant movement, tracers have emerged as powerful tools [4]. For instance, tracers enable clear visualization of water flow paths within the sand filter bed, calculate residence time distribution for different particles or solutes, and provide crucial data for validating computational models simulating sand filtration processes. Thus, tracers could contribute significantly to the understanding of hydrological dynamics within the treated water system [5,6]. Previous studies have effectively employed conventional tracers, such as dyes, fluorescent compounds, and isotopes, in the pursuit of these insights. However, their limitations, including environmental concerns, poor stability, and potential interference with the filtration process [7,8], necessitate exploring alternative tracers for specific applications. Additionally, other studies have utilized tracers, such as silts and silica nanoparticles, to investigate the breakthrough transport characteristics of colloidal particles. Nonetheless, the elimination and quantification of these particles still present challenges that

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need to be addressed. In addition, it is important to highlight that a tracer can only mimic either dissolved transport or particulate transport, but not both simultaneously [9,10].

Encapsulated DNA particles have emerged as environmentally friendly and cost-effective tracers for environmental applications [11]. These colloidal particles entail the encapsulation of DNA within protective matrices, primarily silica, ensuring their durability and safeguarding against degradation. However, challenges persist in the efficient separation and precise quantification of these colloidal particles, especially in the presence of complex water matrices containing various chemical and biological contaminants. To tackle this issue, our study is centered on investigating the kinetic transport behavior of novel particles, equipped with a magnetic core to enable magnetic separation, within sand filters under varying water chemistry conditions [12].

Encapsulated DNA particles have gained attention for environmental research [13]. Pang et al. [14] introduces microspheres as surrogates for pathogens in groundwater research. Coating 20 nm carboxylated microspheres with proteins closely mimics pathogen behavior, providing a new approach for studying pathogen transport in groundwater. In another study [15], surrogate particles for rotavirus and adenovirus were developed using 70-nanometer silica nanoparticles. Filtration experiments demonstrated their similarity to the actual viruses in concentration, filtration efficiency, and attachment kinetics. These surrogates remained stable and easily detectable; and therefore, they hold potential as cost-effective tools for studying virus transport in porous media, benefiting water and wastewater treatment, virus migration tracking, and groundwater protection.

The application of encapsulated DNA colloidal particles as particulate tracers in SF systems holds significant potential for advancing our understanding of hydrological processes within these complex systems. Encapsulated DNA tracers possess several advantages, including sufficient species, specificity, environmental friendliness, stable migration, and high sensitivity. They also eliminate most of the challenges associated with conventional hydrological tracers, such as lack of multiplexed, multipoint tracing, and interference of background noise [16]. By using encapsulated DNA particles, researchers can track the movement and fate of water and particulates, enabling the characterization of flow pathways, and retention times [17]. Furthermore, DNA-based tracers can provide valuable information about biogeochemical processes, such as microbial activity and nutrient cycling [18], which play crucial roles in the water treatment efficiency of SF systems [1].

Transport of colloids through fully saturated porous media is commonly described at a macroscopic scale using the advection-dispersion equation, which incorporates a first-order kinetic retention parameter [19,20]. This parameter can be correlated to colloid filtration theory through a mechanistic model that considers factors such as the trajectory of colloids near a collector [21]. Recent studies have identified several factors that can significantly affect the transport of colloids in saturated porous media, including colloid size-dependent dispersion, gravity effects, mechanical equilibrium, maximum retention function, fraction of collector surface area contributing to colloid attachment, hydrodynamic and adhesive torques, concentration-dependent colloid transport, and nanoscale heterogeneity. These factors highlight the complexity of colloid transport and the need for further research to better understand the mechanisms that govern colloid transport in porous media [22,23].

The movement of silica colloids within quartz sand columns can be described by their attachment to the sand, following a first-order kinetic process. This attachment is affected by various factors, including ionic strength, pH, flow velocity of the pore water, and the composition of the collector surface. Additionally, size exclusion effects may also contribute to the transport behavior [24]. It is important to note that silica colloids have the potential to facilitate the transport of contaminants in subsurface environments. Taken together, these physicochemical factors have an impact on the aggregation, deposition, and remobilization of colloidal matter [9]. Hence, it is necessary to examine how the environmental conditions, such as the water chemistry of the infiltrated water, influence the stability and behavior of the DNA tracer. This investigation aims to optimize the utilization of these particles for the characterization of transport of colloidal particles in SF systems.

The primary objective of this study was to investigate the impact of water chemistry, specifically focusing on ionic strength and cation types, on the transport and behavior of our novel silica-encapsulated DNA particles with a magnetic core, SiDNAMag, within porous media. A series of sand column experiments were conducted, introducing SiDNAMag particle suspensions in various chemical solutions. Notably, the novelty of this research lies in the utilization of the newly developed SiDNAMag as a tracer to the particles can be used to map complex pathways and/or do source tracking in SF systems. To complement these experiments and gain further insights, we employed the HYDRUS-1D model for the analysis of the kinetic transport properties exhibited by these colloidal particles.

## 2. Methodology

### 2.1. DNA-tagged silica particle

This study focused on evaluating the potential of SiDNAMag. The behavior of SiDNAMag in different water chemistry solutions during the infiltration process was investigated. The methodology employed in this study comprised several stages (Fig. 1). Firstly, a series of column experiments were conducted, where various water chemistries and solutions with differing ionic strengths were introduced. Subsequently, samples were subjected to magnetic separation to ensure their efficient isolation and accurate quantification of SiDNAMag. Finally, the modeling phase involved the development of breakthrough curves of relative SiDNAMag concentrations and the implementation of kinetic studies using the Hydrus 1D software tool.

SiDNAMag (Fig. S1) used in this study was provided by the Norwegian University of Science and Technology (NTNU). Detailed information regarding the fabrication process and characteristics of these particles can be found in Sharma's work [25]. To summarize, the synthesis procedure involved the co-precipitation of superparamagnetic iron oxide nanoparticles (IONPs) with sizes ranging from 10 to 20 nm in an alkaline solution containing $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ [26]. The surface of the IONPs was chemically modified using various ligands, including CTAB, Na-citrate, TMAH, and TMAPS, to impart different surface functionalities and charges. Subsequently, the IONPs were effectively functionalized with dsDNA (GM5) (Table S1) and encapsulated within a silica shell. The magnetic properties and stability of the resulting SiDNAMag particles were assessed and reported by Sharma et al. [25].

A procedure was established to enable magnetic separation and quantitative measurement of DNA particles that were bound to superparamagnetic iron oxide nanoparticles (IONPs) using the quantitative polymerase chain reaction (qPCR) technique. The development of the protocol involved investigating the impact of various experimental conditions, including sample volume, magnetic separation time, and the washing frequency of samples with MilliQ water, on the efficiency of particle separation. In summary, the magnetic separation protocol entailed subjecting samples to magnetic separation for 30 min, removing sample water (while maintaining sample SiDNAMag) and replacing with MilliQ, followed by resuspending sample SiDNAMag in MilliQ water to minimize any inhibitory effects during the qPCR analysis. This process was repeated twice before collecting the sample for further analysis using qPCR.

### 2.2. Characterization of SiDNAMag

The zeta potential (ζ) of SiDNAMag was determined using a ZetaSizer Nano S instrument (Malvern Institute, UK). The Smoluchowski equation was employed to calculate the zeta potential based on electrophoretic

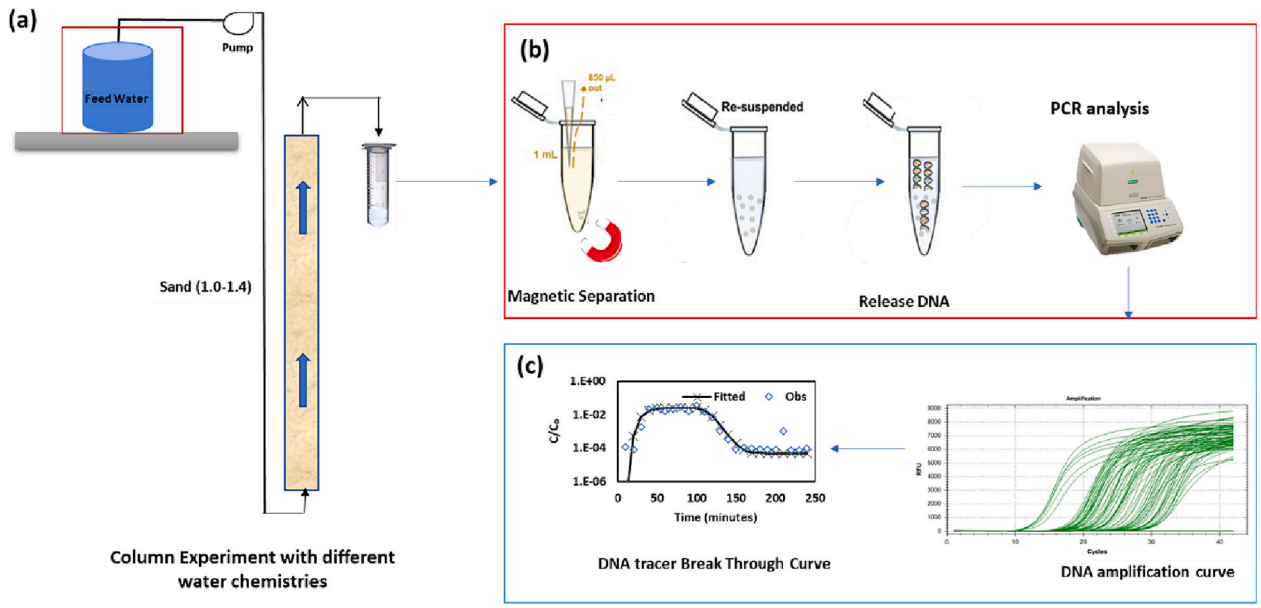


**Fig. 1.** Shows the methodology of the research starting by (a) column experiment fed with different water chemistries and ionic strength solutions, (b) the magnetic separation and quantifying the SiDNAMag particles, (c) modeling and kinetic studies using the Hydrus 1D tool.

mobility measurements of SiDNAMag dispersed in tap water and filtered river water (through a 0.45-μm glass fiber filter). Additionally, the hydrodynamic radius of SiDNAMag was calculated using the Dynamic Light Scattering (DLS) method with a 173° backscattering configuration.

### 2.3. Particle detection and analysis

The analysis of the samples (in triplicate) involved a three-step procedure: sample preparation for quantitative polymerase chain reaction (qPCR), qPCR amplification, and subsequent data analysis, following the method outlined by Tang et al. [27]. Initially, the protective silica was dissolved in the BOE solution, which contained an equal proportion of Ammonium hydrogen Difluoride (NH4FHF) (Sigma Life Sciences) and Ammonium Fluoride (NH4F) (J.T.Baker®), allowing the encapsulated DNA to be released into the liquid medium [24,28]. After adjusting the pH with 0.1 M Tris-HCl, a 5 μL portion of the sample mixture was added to a 15 μL PCR mix. For further details on qPCR conditions, the reader is referred to Tang et al.

### 2.4. Characterization of the sand

The quartz sand utilized in this study was obtained from J.T. Baker, Inc. located in Phillipsburg, New Jersey. The sand was subjected to sieving to obtain fractions within the size range of 1000–1400 μm. The characteristics of the sand can be found in Table S2. The effective porosity of the used sand media was determined following the method of Hao et al. [29], and described in Supplemental information (S1). Prior to introducing the sand into the columns, it underwent a purification process involving overnight soaking in a 10 % HCl acid solution. This treatment aimed to eliminate impurities such as $K^+$, $Ca^{2+}$, $Mg^{2+}$, and $Fe^{3+}$ ions, which could otherwise interact with negatively charged colloidal particles, leading to enhanced retention of SiDNAMag particles [30,31]. The sand was subsequently rinsed multiple times with distilled water to remove any residual particles and acid traces. Afterwards, the acid-washed sand was dried in an oven at 105 °C for 24 h.

To facilitate the packing process and ensure a smooth column, the sand material was treated with carbon dioxide ($CO_2$(g)) in a tightly sealed container. This step served two purposes: it facilitated air removal, and since $CO_2$(g) is more soluble in water than in air, it helped maintain column smoothness by dissolving in the packing water. Experimental assessments revealed that the sand employed in this investigation exhibited an average bulk density of 1500 kg/$m^3$ and a porosity of 0.4.

### 2.5. Column set-up

Four PVC columns were developed and employed in this experiment. Each column had an inner diameter of 0.04 m and a height of 0.1 m. The columns were densely filled with acid-washed silica sand (1–1.4 mm, J. T. Baker, Inc., Phillipsburg, New Jersey) to a uniform height of 9 cm. A 1 cm space was left at the top of each column to ensure homogeneity of the effluent solution. In up-flow mode, a variable-speed peristaltic pump was attached to the base of each column, drawing influent water from a tank at a constant hydraulic loading rate of 0.75 $cm^3$/min (saturated flow).

At regular five-minute intervals, samples were collected from the column outlets using an automatic fraction collector (OMNICOLL Fraction Collector and Sampler, Lambda Laboratory Instruments). Particle samples were subjected to qPCR analysis, while salt tracer samples were examined using an electrical conductivity meter (WTW-Portable conductivity meter ProfiLine Cond 3310). To assess column packing and determine parameters such as porosity and dispersivity, a one-dimensional solute transport code, HYDRUS-1D, was employed [32]. Several tracer experiments using NaCl solution were conducted by injecting 2.5 pore volumes of the solution used for particle injection. After conducting salt tracer transport investigations, SiDNAMag particles, at a concentration of $10^4$ particles/ml, were dispersed within different salt solutions encompassing NaCl, $NaHCO_3$, $CaCl_2$, and $MgCl_2$, characterized by ionic strengths spanning from 0.1 mM to 20 mM. The SiDNAMag particle suspensions were sequentially introduced into the four columns, with each column dedicated to a specific salt type. Subsequent to each injection experiment, the columns were subjected to a regimen of four pore volumes of background salt solutions. Subsequently, an extensive flushing protocol was implemented, which entailed the use of Milli-Q (MQ) water for several days, ensuring complete removal of residual particles and salts before proceeding to the subsequent experiment employing a higher ionic strength solution. The physical and chemical properties of the feed and effluent water, such as pH, temperature, dissolved oxygen, and electrical conductivity, were monitored to verify the columns were operating under the desired

conditions.

### 2.6. Modeling of transport of DNA-tagged silica particle

An advection-dispersion equation that includes colloid attachment and de-attachment from and to the aqueous phase was used to describe colloidal particle transport in saturated porous media. The governing equation in one-dimension is written as follows [33]:

$$\frac{\partial C}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial S}{\partial t}=\lambda_L v\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial \mathrm{EQ}\,x}\ \mathrm{EQ} \tag{1}$$

$$\rho_b\frac{\partial S}{\partial t}=k_{att}\theta C-k_{det}\rho_b S \tag{2}$$

In these equations, $C$ [$ML^{-3}$] represents the concentration of colloids in the aqueous phase, $S$ [$MM^{-1}$] represents the concentration of colloids on the solid phase, $\rho_b$ [$ML^{-3}$] is the dry bulk density, $\theta$ [$M^3M^{-3}$] is the volumetric water content, t [T] is time, L [L] is the dispersivity, $v$ [$MT^{-1}$] is the pore water velocity, $x$ [L] is the distance, $k_{att}$ and $k_{det}$ [$T^{-1}$] are the first-order attachment and detachment rate coefficients, respectively.

We employed HYDRUS-1D to determine dispersivity, porosity, attachment and detachment rate coefficients [34]. The dispersivity and porosity values were obtained by fitting NaCl tracer data, while the first-order attachment and detachment rate coefficients were determined using the relative breakthrough data of SiDNAMag, with the porosity and dispersivity values derived from the NaCl tracer experiment. The code was configured to consider log-resident concentrations, disregarding colloid size-dependent dispersivity and mechanical equilibrium. This approach led to an underestimation of colloid dispersivity. Additionally, gravity effects were excluded due to the small size of SiDNAMag, resulting in negligible restricted settling velocity based on column orientation and flow direction [9]. The presented model (Eqs. (1), (2)) is implemented in the HYDRUS-1D software package. The spatial discretization employed a Galerkin-type linear finite element method, temporal derivatives were approximated using finite difference methods, and the advection-dispersion equation was solved using the Crank-Nicholson finite difference scheme [35]. Parameter optimization involved defining an objective function and minimizing it using the Levenberg-Marquardt nonlinear minimization method, which utilizes a weighted least-squares approach based on Marquardt's maximum neighborhood method [36].

The sticking efficiency ($\alpha$) is a measure of the proportion of SiDNAMag nanoparticles that attach to the surface of a sand particle compared to the total number of nanoparticles that collide with the surface. A sticking efficiency of 0 indicates that no nanoparticles adhere to the surface, while a sticking efficiency of 1 means that all colliding nanoparticles adhere. The dimensionless sticking efficiency was calculated using the following equation:

$$\alpha=K_{att}\frac{2d_g}{3(1-\varepsilon)\nu\eta_o} \tag{3}$$

Here, $d_g$ represents the diameter of sand grain [L], $\varepsilon$ denotes porosity of sand column [−], and $\eta_o$ refers to the single collector efficiency [−]. The $\eta_o$ was calculated using the formula provided by Tufenkji and Elimelech [37], where the particle density of the SiDNAMag particle is considered 2500 kg/$m^3$ and the Hamaker constant, a coefficient accounting for the van der Waals interaction between the two materials, was assumed to be $5\times10^{-20}$ J. The attachment rate coefficient $K_{att}$ was determined through HYDRUS modeling.

## 3. Results

### 3.1. SiDNAMag characterization

To assess the stability of DNA-tagged silica particles (SiDNAMag), we conducted measurements of their hydrodynamic diameter and zeta potential (ζ) in various water chemistry solutions at pH 6.8–7.3 and 25 °C. We found that SiDNAMag formed aggregates when suspended in Milli-Q water, resulting in a hydrodynamic diameter of 550–670 nm. In solutions with higher ionic strength (0.1–20 mM), the hydrodynamic diameter increased to 700–900 nm. The zeta potential in Milli-Q water ranges from −17 to −18 mV. As the ionic strength of the solution increased from 1 mM to 20 mM, the ζ value increased from −25 to −6 mV. This observation signified that the SiDNAMag particles carried a negative charge under varying water chemistry conditions. Also, the ζ value did not exceed the conventional threshold of 20 mV for colloidal stable suspensions, which suggested that aggregation could occur.

### 3.2. Column breakthrough curves (BTCs)

Initially, the columns underwent a NaCl solution run, with an electric conductivity (EC) of $2.5\times10^3$ μs/cm. The injection of the saline solution continued for 2 pore volumes (PV) until the relative concentration $(C/C_0)_{EC}$, where C represents the effluent EC-value (indicative of sodium chloride concentration) and $C_0$ represents the influent EC-value, reached 1. Subsequently, the columns were flushed with Milli-Q water for 4 PV to elute the salt. The form of the NaCl tracer breakthrough curve further confirmed the appropriateness of the column setup in all cases, exhibiting no leakage and a front displacement perpendicular to the flow direction (Fig. 2.a). To model the NaCl injection breakthrough curve and estimate the properties of the sand, the Hydrus-1D software tool was employed. The estimated values for porosity ($\varepsilon$) and hydraulic conductivity (Ks) were determined to be 0.08 cm/min and 0.4, respectively. The porosity values obtained through the gravimetric method ranged from 0.36 to 0.4, aligning well with the data derived from the model. The longitudinal dispersivity (D) for the four columns was calculated to range from $2.2\times10^{-1}$ cm to $1.9\times10^{-1}$ cm. Given the substantial Peclet number value (Pe > 1), indicative of advection's prominent role in the transport process, we have utilized the dispersivity of the conservative tracer for the fitting of SiDNAMag breakthrough curves [38].

### 3.3. Breakthrough curves of SiDNAMag in different solutions

In a series of experiments using saturated soil columns, we investigated the influence of various solutions (MILLI-Q water, NaCl, $NaHCO_3$, $CaCl_2$, and $MgCl_2$) with ionic strengths ranging from 0.1 mM to 20 mM on the transport of SiDNAMag. The breakthrough curves (Fig. 2), which represent the normalized effluent concentrations (C/C0) of SiDNAMag over time in minutes, were analyzed. The pH of the effluent from columns fed with NaCl, $CaCl_2$, and $MgCl_2$ solutions of different ionic strengths ranged between 6 and 7.2. However, for columns fed with $NaHCO_3$, the effluent pH varied from 8.2 to 9.5. Upon injecting SiDNAMag particles into Milli-Q water, $(C/C0)_{SiDNAMag}$ rapidly increased and reached a plateau phase with a maximum value of 0.1 after 1.5 pore volumes (PV). During the elution phase (after PV 3.5), $(C/C0)_{SiDNAMag}$ in Milli-Q water sharply decreased and stabilized at $1\times10^{-4}$ after 4 PV. The qPCR analyses reached the detection limit when $(C/C0)_{SiDNAMag}$ approached $1\times10^{-4}$. The transport behavior of SiDNAMag was similar for NaCl and $NaHCO_3$ solutions, where the rise period, rising limb, plateau phase, and declining limb were comparable to those observed in MILLI-Q water. However, the breakthrough curve of SiDNAMag in $CaCl_2$ and $MgCl_2$ showed a slower rise compared to the initial rise in Milli-Q water.

The $k_{att}$ and $k_{det}$ parameters were employed to fit the curve using the HYDRUS code. We observed a close match between the experimental data and the fitted models for all water chemistries tested, which was consistent with previous findings on the transport of silica particles through homogeneous and heterogeneous soil columns [22,39]. With the exception of the $MgCl_2$ experiment at an ionic strength of 1 mM, which exhibited poor breakthrough, all SiDNAMag breakthrough curves (BTCs) could be reasonably fitted, with $R^2$ values ranging from 0.42 to 0.88. Overall, the kinetic characteristics indicated that SiDNAMag had a

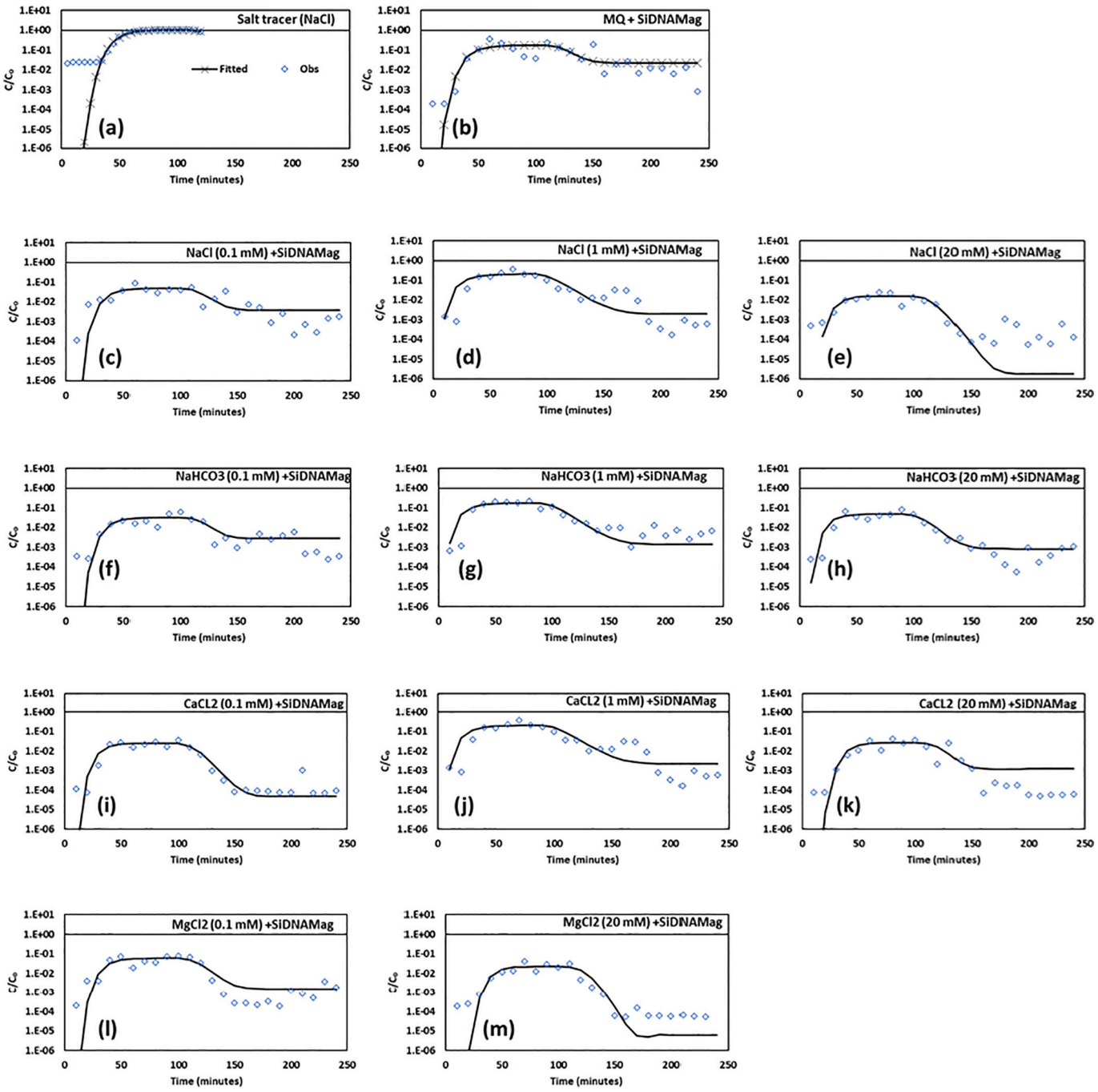


**Fig. 2.** Experimental data of NaCl tracer, SiDNAMag (symbols) and fitted breakthrough curves with HYDRUS (lines). Different panels illustrate relative concentrations as a function of time (minutes) within the sand columns. Column height (10 cm), diameter (2.5 cm), sand size (1–1.2 mm), Darcy velocity (785 m/y). The columns fed with different chemistry solutions (NaCl, NaHCO3, CaCl2 and MgCl2) with different ionic strength (0.1, 1, 20 mM).

higher attachment rate (at least two orders of magnitude) compared to the detachment rate. The attachment and detachment characteristics of DNA particles on the surface of sand grains did not exhibit a distinct pattern with ionic strength within the range of 0.1 to 1 mM. However, SiDNAMag exhibited significant attachment and low detachment rates in high ionic strength solutions (20 mM). The lowest attachment rate was observed when MilliQ-water was used as the background solution, with a $k_{att}$ value of $3.7 \times 10^{-2}$ (Table 1). Solutions with an ionic strength of 20 mM exhibited the highest $k_{att}$ values (ranging from $8.0 \times 10^{-2}$ to $9.5 \times 10^{-2}$) and the lowest $k_{det}$ rates (ranging from $1.8 \times 10^{-4}$ to $8.4 \times 10^{-8}$).

The kinetic data obtained from the experiments was utilized to estimate the sticking efficiency of SiDNAMag particles on sand grains under different experimental conditions, using Eq. (3). The results consistently demonstrated a relatively high sticking efficiency across all chemical solutions tested. Remarkably, the lowest observed sticking efficiency value of 0.53 was obtained when SiDNAMag particles were suspended in MilliQ water. This finding indicated that over 50 % of the particles involved in the collision process, defined as SiDNAMag colliding with the sand surface, effectively adhered to that sand surface, highlighting a significant ratio of collisions resulting in sticking. The sticking efficiency for chemical solutions with varying ionic strengths (ranging from 0.1 to 20 mM) ranged from 0.7 to 1.0 (Fig. 3). These findings suggested that a substantial proportion of SiDNAMag particles

**Table 1**
HYDRUS model param, attachment katt [$min^{-1}$], detachment kdet [$min^{-1}$], and sticking efficiency param of SiDNAMag calculated by curve fitting for different solutions (NaCl, NaHCO3, CaCl2, and MgCl2) at different ionic strengths 0.1, 1 and 20 mM.

| Chemical solution | Ionic strength [mM] | $R^2$ | $k_{att}$ [$min^{-1}$] | $k_{det}$ [$min^{-1}$] |
|---|---|---|---|---|
| MilliQ-water | | 0.68 | 3.7E-02 | 9.9E-04 |
| NaCl | 0.1 mM | 0.69 | 8.9E-02 | 2.5E-04 |
| | 1.00 | 0.79 | 4.3E-02 | 9.0E-05 |
| | 20.00 | 0.77 | 9.5E-02 | 3.1E-07 |
| $NaHCO_3$ | 0.1 mM | 0.64 | 1.3E-01 | 1.5E-04 |
| | 1.00 | 0.88 | 5.0E-02 | 7.2E-05 |
| | 20.00 | 0.80 | 8.0E-02 | 8.5E-05 |
| $CaCl_2$ | 0.1 mM | 0.46 | 8.7E-02 | 8.2E-06 |
| | 1 | 0.49 | 4.4E-02 | 7.6E-04 |
| | 20 | 0.65 | 7.8E-02 | 1.8E-04 |
| $MgCl_2$ | 0.1 mM | 0.78 | 6.3E-02 | 1.3E-04 |
| | 1 | – | 3.3E-02 | 3.3E-07 |
| | 20 | 0.74 | 7.9E-02 | 8.4E-08 |

tended to adhere to the surface of sand during the infiltration process, regardless of the specific types of ions present in the solution.

## 4. Discussion

This study focused on investigating the sensitivity of SiDNAMag which had a magnetic iron core to facilitate separation and quantification, to solution chemistry, while elucidating the underlying mechanisms governing their transport and retention. Through laboratory investigations, we conducted a detailed analysis of the behavior of DNA-tagged silica particles in relation to solution chemistry during the sand filtration processes. Additionally, we employed breakthrough curve analyses using HYDRUS-1D modeling to gain a comprehensive understanding of the transport dynamics involved. Our findings suggested that the transport of SiDNAMag in saturated sand columns could be effectively described by employing a first-order kinetic attachment and detachment rate coefficient. These kinetic transport characteristics of silica nanoparticles have been previously observed in several studies [40–43]. For instance, Chakraborty et al. [44] investigated the influence of initial concentration ($C_o$) of silica-DNA-silica (SiDNASi) nanoparticles (ranging from $8.7 \times 10^2$ to $6.6 \times 10^8$ particles $ml^{-1}$) on their transport behavior within a 15-cm column filled with saturated quartz sand. Chakraborty et al. revealed a notable increase in the maximum relative effluent concentration with higher $C_o$, as indicated by the breakthrough curves (BTCs) that exhibited a 2-log rise. Moreover, they demonstrated a decrease in the logarithm of $k_{att}$ with increasing $C_o$, indicating a decrease in the efficiency of single-collector removal (η). This decline in η can be attributed to various factors, including enhanced electrostatic repulsion between colloids in the aqueous and solid phases, the formation of shadow zones downstream of deposited colloids, and the removal of loosely attached colloids from the solid phase (quartz sand). Collectively, these factors contributed to an increased occurrence of inter-colloidal collisions between SiDNASi particles in the aqueous and solid phases as the concentration of SiDNASi increased. However, it is important to acknowledge that other factors such as diffusion limitations, steric hindrance, or the presence of competing reactions can also influence the overall kinetics of attachment [45].

The kinetic parameters governing the behavior of silica colloids are strongly influenced by the ionic strength and pH of the infiltrating water. Our study revealed that increasing the ionic strength of the feedwater had a dual effect: it enhanced the attachment rate and reduced the de-attachment rate of SiDNAMag particles. As the ionic strength of the solution decreased to 0.1 mM during the infiltration process, a significant 1–2 log removal of SiDNAMag particles was observed. A study conducted by Zeng et al. [40] examined the impact of ionic strength on the transport and retention of $SiO_2$ nanoparticles (NPs) in three commonly used porous materials, namely sand, anthracite, and granular activated carbon (GAC). The study employed a first-order kinetic mechanism to describe the transport kinetics of silica NPs in different filter media. The findings indicated that increasing ionic strength promoted NP agglomeration and facilitated $SiO_2$ NP retention, while low ionic strength resulted in the release of captured NPs from the sand bed. Anthracite and GAC exhibited a higher affinity for SiO2 NP capture compared to sand, primarily due to their porous structure and larger surface area. However, our research revealed notable discrepancies between the experimental data and the fitted model when higher ionic strength solutions (20 mM) were used as infiltrating water. To address these discrepancies, more advanced models incorporating factors such as two kinetic sites, gravity effects, colloid-size dependent dispersivity, and nanoscale heterogeneity are likely necessary. By integrating these complexities into the models, we can enhance the accuracy of predicting the behavior and transport of DNA-tagged silica particles in porous media [46]. Samari-Kermani et al. [47] used the Lattice Boltzmann-Smoothed Profile technique to model particle interactions and their response to ionic strength. Key assumptions in their simulations were: (i) Simulations considered particle sizes of 3, 5, and 10 μm, and therefore negating the impact of molecular diffusion. (ii) They assumed uniformly charged, chemically homogeneous surfaces without roughness on both particles and pore surfaces. Furthermore, the author employed the sphere-plate equation to calculate particle-surface

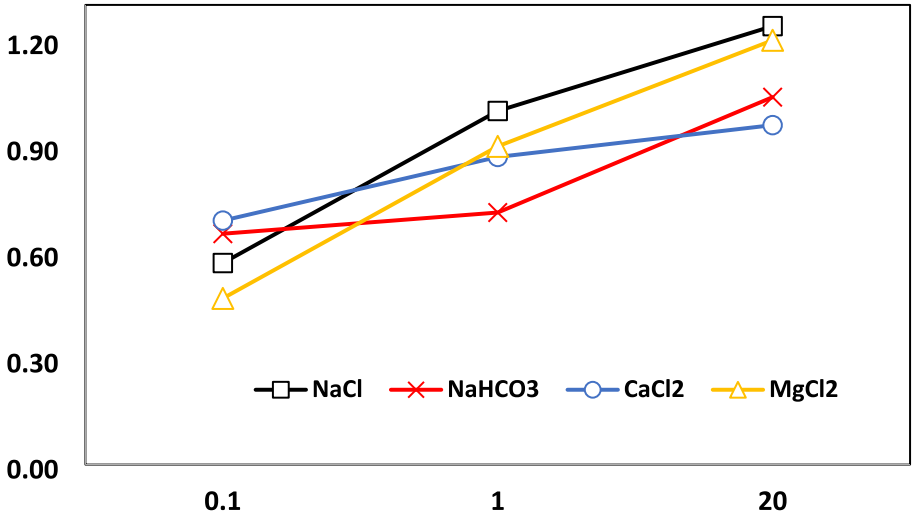


**Fig. 3.** Calculated sticking efficiency ($\alpha$) values of SiDNAMag as a function of ionic strength (mM).

interactions. The study revealed that increasing ionic strength had a more significant impact on particle behavior than increasing zeta potential. Specifically, higher ionic strength led to a decrease in pore void fraction and conductivity, as well as an increase in aggregate connectivity.

Sticking efficiency was utilized as a metric to quantify the ratio of colloids adhering to the surface of sand grains to the total number of colloids colliding with the surface. It is important to recognize that sticking efficiencies >1 are not physically possible since the proportion of particles attaching to the sand grain surface cannot exceed the total fraction of DNA colloids interacting with the surface. This limitation arises from the irregular shapes of the silica grains acting as collectors. The correlation equation employed to estimate the single collector efficiency was originally developed for spherical collectors and may have introduced inaccuracies in assessing sticking efficiencies due to the non-uniform shapes of the collector grains. Nevertheless, the calculated sticking efficiencies consistently indicated that a significant proportion, and in some cases, the entire population of DNA colloids colliding with the sand grain surface exhibited adhesion, highlighting a pronounced tendency for sticking in our experimental setup. Importantly, previous studies [9,44,48] have also reported high sticking efficiency of Si-nanoparticles on sand grains. In a previous study, Kianfar et al. [9] investigated the influence of water chemistry on the sticking efficiencies of SiDNASi particles (particle size = 270 nm, zeta potential = −42.5) within 6.5 cm height sand columns. The research revealed that the sticking efficiencies in demineralized water ranged from 0.0008 to 0.27, while approaching unity when the colloidal particles were suspended in NaCl and $CaCl_2$ solutions. In our current investigation, the remarkable high sticking efficiency observed for SiDNAMag particles suspended in MilliQ water can be ascribed to the particle charge. Silica colloidal particles with elevated negative zeta potentials tend to manifest stronger repulsive forces, leading to reduced attachment rates [49]. Conversely, colloids with zeta potential values exceeding −20 mV are considered unstable [9], exhibiting a tendency to aggregate in the medium. This aggregation process is particularly pronounced in solutions with higher ionic strength values [50]. This explained the increased sticking efficiency observed for SiDNAMag, which possesses a magnetic core and retained similar characteristics to SiDNASi, in the MilliQ water suspension. Wang et al. [41] applied the DLVO theory and observed that a notable portion of the DNA colloids retained on the sand grain surface occupied the secondary energy minimum, resulting in increased retention levels. Understanding the relationship between particle charge and sticking efficiency is crucial in elucidating the mechanisms governing colloidal particle behavior in sand filtration systems. The findings underscore the importance of surface properties in influencing colloidal particle interactions with sand grains, offering valuable insights for applications such as water treatment and filtration processes.

The present study's findings underscore the potential of SiDNAMag in sand filtration systems mapping complex pathways and/or do source tracking. [11,51,52] and the fate of particulates. The incorporation of a superparamagnetic iron core enhanced their separation and quantification, even at extremely low concentrations [28]. However, the observed significant sticking efficiency of these colloids may impede their effectiveness as conservative tracers. To mitigate this issue, strategies to enhance the negative charge on the colloidal particle surface and reduce the effect of positive charge holder elements in the medium are proposed. We speculate that the application of humic compounds could counteract the negative impact of cations on the transport of silica DNA particles [53,54], thereby increasing the mass recovery of the Si-colloidal particles. Furthermore, modifying the surface properties of silica nanoparticles presents a feasible approach to alter their interactions with sand grains and reduce attachment. Various surface functionalization techniques involving repulsive agents or coatings, such as polymers or surfactants [55,56], have been proposed in the literature to address aggregation and binding concerns of silica nanoparticles. These techniques include applying a hydrophilic coating to the nanoparticle surface, introducing negatively charged functional groups like carboxyl (-COOH) or sulfate (-SO3H) [57], and attaching zwitterionic molecules, such as SB3–14 (sulfobetaine 3–14) and NDSB 201 (pyridinium propylsulfonate-(1)), to create a neutral and hydrophilic surface [58–60]. These approaches have shown promise in reducing aggregation and sticking efficiency of silica nanoparticles. The implementation of such surface modification techniques can contribute to the advancement of colloidal tracers in sand filtration studies, fostering their practical applications in water treatment and filtration processes.

While our research has furnished valuable insights into the utility of SiDNAMag particles as tracers in sand filtration systems, it is prudent to acknowledge certain limitations inherent in our approach. Most notably, these synthetic particles may exhibit constraints in faithfully representing the diverse nature of natural colloids. Although our SiDNAMag particles closely approximate certain properties of specific natural colloids, such as size, charge, and surface characteristics, it is imperative to recognize that natural colloids are characterized by a rich spectrum of attributes contingent upon their composition and origin. The inherent variability in factors such as size distribution, surface chemistry, and steric interactions within natural colloid populations may give rise to transport behaviors that deviate from those of our engineered particles. Consequently, while our study underscores the potential of SiDNAMag particles as effective tracers, it's imperative to acknowledge that their universality in emulating the full spectrum of natural colloids may be limited. To attain a more comprehensive understanding of colloid transport in porous media, future investigations should encompass the broader landscape of colloidal diversity and account for the multifaceted interplay of various components within natural systems.

## 5. Conclusion

In conclusion, this study has shed light on the sensitivity of SiDNAMag particles to solution chemistry and the underlying mechanisms governing their transport and retention in sand filtration systems. Our findings have contributed to a better understanding of the transport dynamics of DNA-tagged silica particles in porous media and their potential as tracers. The kinetic parameters governing the behavior of these synthetic particles are significantly influenced by the ionic strength and pH of the infiltrating water. These findings have implications for various applications, including groundwater studies, water and wastewater treatment, and groundwater protection. However, the study also highlighted certain limitations. While SiDNAMag particles closely emulate specific natural colloids, the diversity of natural colloids in terms of size, surface properties, and steric effects can lead to differing transport behaviors. This suggests that SiDNAMag particles may not be universally applicable as tracers for all natural colloids. Future research should explore a wider range of colloidal diversity and consider the multifaceted interactions in natural systems to comprehensively grasp colloid transport in porous media. Additionally, the high sticking efficiency observed for SiDNAMag particles in certain conditions may affect their use as colloidal tracers. Potential strategies to mitigate this limitation include modifying particle surface properties and employing surface functionalization techniques. In general, this study underscores the potential of SiDNAMag particles while acknowledging the need for further research to address the highlighted limitations and enhance their practical applications.

## CRediT authorship contribution statement

**Ahmed Abdelrady:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yuchen Tang:** Writing – review & editing, Visualization, Validation, Methodology. **Thom Bogaard:** Writing – review & editing, Supervision, Resources, Funding acquisition, Formal analysis, Conceptualization. **Jan Willem Foppen:** Writing – review & editing, Supervision, Resources, Project administration, Funding

acquisition, Formal analysis, Conceptualization.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Thom Bogaard reports financial support was provided by NWO. Thom Bogaard reports financial support was provided by European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2024.105316.

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