

Effect of pH for Colloid Stability in Chemically Heterogeneous Soils

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Abstract—Until recently, natural soils were believed to constitute two mobile phases: soil moisture and soil air. However, research revealed later the presence of another mobile phase, which is now referred as the colloidal phase, with a strong potential to facilitate the transport of toxic contaminants and various nutrients to groundwater, leading to significant health concerns. Colloids, consisting of soil particles of nano and micrometer scale, are highly reactive in subsurface and sensitive to the physico-chemical properties of soil, including soil pH. This study investigated the effect of pH on colloid transport using soil samples collected from two agricultural lands in Medawachchiya and Horowpathana in North Central Province of Sri Lanka, which were recognized as high-CKDu endemic and low-CKDu endemic areas, respectively. Stability of the colloids extracted from the two soil was investigated by varying the pH as 3, 5, 6, 7, 8, 11 in room temperature. According to the results, enhance colloid stability at higher pH values was observed for both soil types. Furthermore, colloid turbidity change with time was numerically characterized and parameterized with an exponential parametric function. These findings could be used effectively on controlling groundwater contamination via colloid-facilitated transport in subsurface in contaminated soils.

Keywords—colloids, colloid stability, colloid-facilitated transport, pH, groundwater

I. INTRODUCTION

Soil is generally considered to be a three-phase system wherein solid particles, soil water and soil gas coexist. Solid particles are evidently immobile while the other two phases, soil moisture and soil gas, are mobile. However, as a result of extensive research carried out by various researchers for several decades, another mobile phase was identified and denoted as the colloidal phase which potentially carry contaminants in subsurface [1, 2, 3, 4 and 5]. Colloids consist of small particles of

nano and micrometer scale which are capable of sorbing organic and inorganic contaminants and stabilize them in the mobile phase [1]. They potentially facilitate transport of numerous contaminants in soil including radionuclides, hydrophobic organic compounds (HOCs), heavy metals, pesticides, pathogens etc. Colloids are technically defined as substances which consist particles substantially larger than atoms or ordinary molecules but too small to be visible to the unaided eye. Literature provides various definitions to the particle size of the colloids as 1 μm to 1 nm [2], <1 μm [3], <10 μm [1, 4], 10 μm – 10 nm [5, 6] as well as 1 μm -10 nm [7].

Characteristically, colloids have two important attributes which make them so influential to groundwater; the high charge, and the large specific surface area (i.e., surface area per unit mass). Owing to these two attributes, they can adsorb a wide range of charged contaminants, and carry them to groundwater faster than the dissolved contaminants do. This process is called ‘Colloid-Facilitated Transport (CFT)’. The mobilization and transport of colloids, and migration of colloid-facilitated contaminants in subsurface is a significant field of study as this process could contribute to the contamination of groundwater with toxic contaminants such as heavy metals (e.g., Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Thallium (Tl), and Lead (Pb), Nickle (Ni)) and eventually a cause for various health effects.

Chronic Kidney Disease of unknown etiology (CKDu) can be identified as a widely affected health problem in North Central province of Sri Lanka. Though not conclusively stated, heavy metals were supposed to play a role in the CKDu problem. Another major attribute of heavy metals for health effects is their non-biodegradability and bio-accumulative behavior. Many heavy metal ions, such as Hg, Cd, Pb, Ni, and Cr, are tend to accumulate in living organisms and also known to be very toxic or carcinogenic [8]. Therefore, an agricultural land was selected as the study area which was used for agricultural purposes for several decades with applications of fertilizers and

agrochemicals such as pesticides, weedicides, glyphosate etc.

In general, colloids are formed by physico-chemical perturbations in groundwater, artificial groundwater recharge, anoxic and oxic groundwater mixing or contaminant plumes leaching from waste disposal facilities. Such plumes can lead to strong gradients in ionic strength, ionic composition, contaminant concentrations and redox potential. The major source of mobile colloids in groundwater is generally considered to be the in-situ release of colloids [10] mobilized due to the changes of hydro-geochemistry of groundwater. Colloids can potentially remain suspended in pore waters for a long time under favorable geochemical conditions without coagulation. Changes in solution chemistry promote colloid mobilization mainly by altering the double layer potential energy due to decreasing the ionic strength of the electrolytic solution, adsorption of ions and macromolecules that alter mineral surface charge, etc. [11].

Moreover, the mobility/transportability of in-situ colloids and colloid-facilitated contaminants are highly sensitive to the physical properties of soil and geochemistry of soil water. Hydraulic conductivity, dispersivity, particle-size distribution, soil pH and electrical conductivity, stability of colloids, elemental composition, specific surface area, pore size and geometry of the actively conducting pore system [10] can be stated as some of the dominant physico-chemical properties which could affect this phenomenon. Among those properties, pH was selected in this study to investigate the effect of pH condition on the under-explored transport domain of colloids and contaminants. Generally, the amphoteric minerals are positively charged at lower pH values and negatively charged at higher pH values. The attractive double layer potentials between oppositely charged surfaces can be made repulsive if a change in solution chemistry reverses the surface charge of one of the surfaces [12]. Extensive experimental studies revealed that the increases in pH enhance the release rate and increases in the total amount of particles released. It leads to high repulsive forces that drive colloid release [13].

Despite many research studies from multiple perspectives on the CKDu problem in NCP of Sri Lanka, no systematic study has undertaken to investigate the potential of soil colloids on groundwater transport of contaminants. This study

investigated the effect of pH on colloid stability in heterogeneous soil-water system from soils sampled from an agricultural land in Madawachchiya where notable number of CKDu patients were recorded and also in Horowpathana where less number of reported patients (as reference), both districts belong to the NCP of Sri Lanka.

II. MATERIALS AND METHODS

A. Materials

Soil colloids were extracted from undisturbed soil samples which were collected from (1 m average depth) highly CKDu affected area in North central province in Medawachchiya (referred hereafter as high-endemic soil) and also from a less-affected area in Horowpothana (referred hereafter as low-endemic soil) where the higher number of CKDu patients and relatively lower number of CKDu patients have been reported, respectively [14]. HNO₃ and NaOH were used for pH adjustments. Further, NaCl was used as a tracer element in column experiments to mimic the water flow through the column. All these chemicals used were of analytical grade.

B. Methods

First, the colloidal solutions were prepared by air drying the soil, sieved by 2 mm sieve, and 150 g of sieved soil was shaken manually [15] in 1-L water for 15 minutes in order to break the soil aggregates. Next, the soil solution was kept undisturbed for 20 hours at 25°C. The fraction with Stokes' diameter < 2µm was filtered out and used as the colloidal solution. The pH of the solutions was adjusted as 3, 5, 6, 7, 8, 11 using HNO₃ and NaOH. Then, the turbidity was measured (Hach Benchtop 2100N Laboratory Turbidimeter, EPA, 230 Vac) at predefined time intervals to obtain the colloid concentration.

Moreover, comparison of specific surface area (SSA) of high endemic and low endemic soil was done using the BET (Brunauer, Emmett and Teller) analyzer. X-Ray Powder Diffraction (XRD) analysis was carried out to identify the phases of the material and to obtain the information on unit cell dimensions. The soil samples were ground to obtain particles under 45 µm before they examined by the XRD. Particle Size Distribution Analysis (PSD) was conducted using sieve analysis and hydrometer methods. As mentioned in [16], Point of Zero Charge was determined using the salt addition method where pH of 0.01 M NaNO₃ was adjusted to values

between 2 – 11 using 0.1 M HNO₃ or 0.1 M NaOH. Then, 0.2 g of soil sample was added to 40 ml of the pH adjusted solution and kept for 24 hours at 150 rpm. Final pH was measured and plotted against the difference in initial and final pH values.

C. Numerical Modelling

Colloid turbidity change with time was numerically characterized and parameterized with an exponential parametric function as shown in (1).

$$N(t) = N_{t=\infty} + (N_{t=0} - N_{t=\infty}) e^{\ln(0.9)(\frac{t}{t^*})^p} \quad (1)$$

where $N_{t=\infty}$ is the turbidity of the colloidal solution after infinitely larger time period (NTU), $N_{t=0}$ is the initial turbidity of the solution (NTU), t^* is the characteristic time at which the turbidity of the suspension is dropped by 90% of its initial turbidity (min) and p is a shape factor which accounts for the curvilinearity of the curve.

III. RESULTS AND DISCUSSION

A. Characterization of soil and colloids

Table I shows the properties of soil and soil colloids used in the experiments. Bulk density and particle density values of high endemic and low endemic soils are comparatively same. Compared to the low-endemic soil, high-endemic soil shows higher SSA of 2650 cm²/g. The higher SSA of high-endemic soil could be considered as an evidence for the higher adsorption capacity of high-endemic soil for in-situ heavy metal ions. Fig. 1 shows the particle size distribution (PSD) curves for two soil types and the D_{50} values obtained from the particle size distribution curves are also shown in Table I. Both soils showed close D_{50} values as well as similar size distribution of particles.

In the particle size distribution curves, the symbols represent the experimental data while the

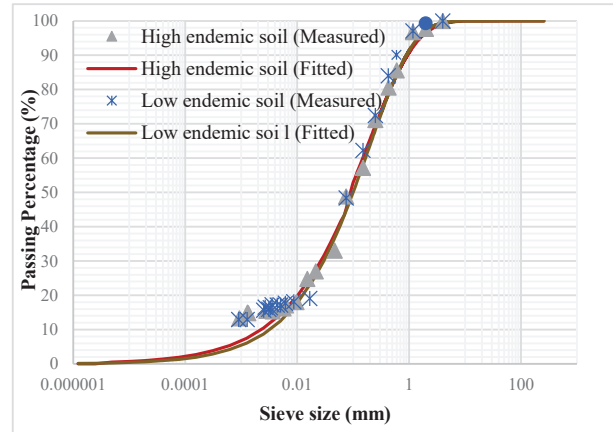


Fig. 1. PSD curves

solid lines give model predictions which were fitted to the modified Rosin Rammler equation [17] as shown in (2).

$$p(x) = 100 [1 - e^{-\ln 2 (\frac{x}{D_{50}})^\beta}] \quad (2)$$

where x is the particle size, D_{50} is the mean particle diameter and β is an empirical constant of the distribution. Moreover, the particle size of both colloidal samples are less than 10 μ m hence they can be technically considered as the colloidal samples.

Fig. 2 shows the X-Ray powder diffraction analysis (XRD) for two soil types and it showed five and four major compound in high and low-endemic soils respectively. High-endemic soil consists of Graphite Hydrogen Nitrate, Di (μ -4,4'-bipyridinesilver) nitrate, Albite, calcian, ordered, dibarium cobalt dichloride bis (selenate(IV)) and Potassium Iodate. Low-endemic soil consists of α -PEN or α -Poly (ethylene-2,6-naphthalate), (Isothiocyanatomethylene) dibenzene, 2-Thiohydantoin, Nylon 6,3.

Therefore, it can be concluded that the heavy metals are not naturally occurred in both soils and they could be only contaminated by various anthropogenic activities such as intensive use of

TABLE I. CHARACTERIZATION OF SOIL AND COLLOIDS

Soil Type	Bulk Density (g/cm ³)	Particle density (g/cm ³)	D ₅₀ from PSD curve (mm)	Initial moisture content (%)	Electrical conductivity (μ S/cm)	pH	Organic matter content (%)	Specific surface area (cm ² /g)	Point of Zero charge
High-endemic	1.70	2.65	0.100	2.64	250-300	6.5-7.6	1.31	2650	6.5-7.0
Low-endemic	1.69	2.63	0.098	4.37	150-220	6.5-7.9	3.34	1870	6.5-7.0

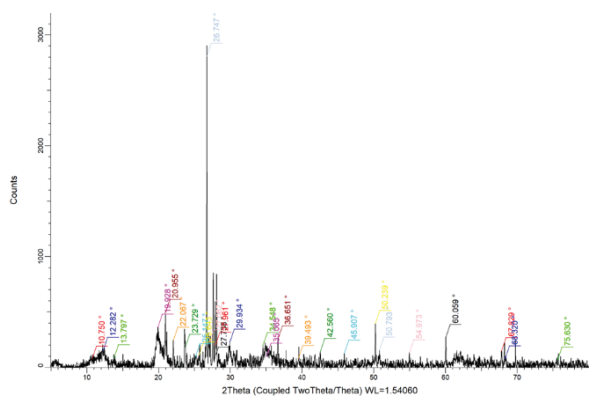


Fig. 2. XRD curves

fertilizers, pesticides, weedicides and several other agrochemicals such as glyphosate which contain heavy metals.

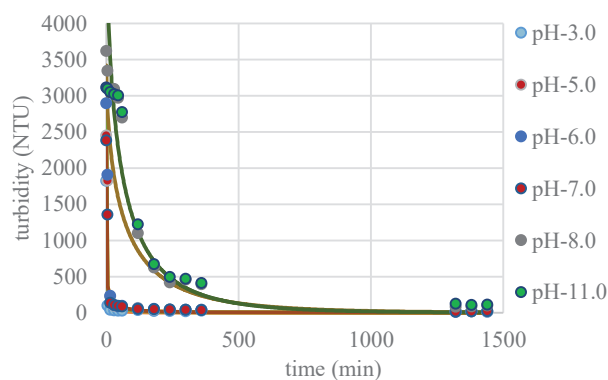
Point of Zero Charge (PZC) values for both soil types were around 6-7 pH. However, according a study done by Appel *et al.*, 2001 [18], points of zero charge for kaolinite and synthetic goethite were found in the ranges of 2.7 – 3.2 and, 7.4 – 8.2, respectively. These differences could be due to the variations in the physico-chemical properties of soil.

B. Colloid stability tests

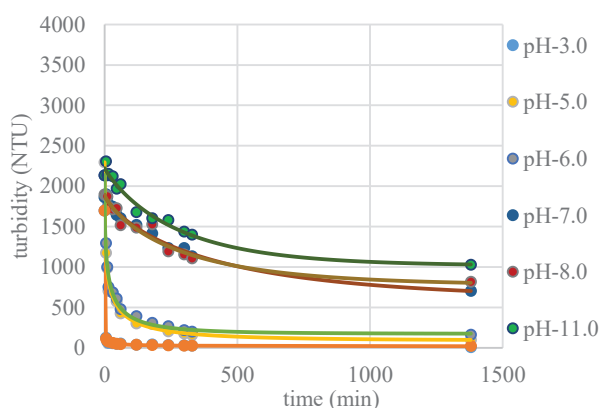
Investigating the stability of colloids has a significant importance when studying colloidal behavior in subsurface. The colloid-facilitated contaminant migration processes are significantly affected by colloidal stability. The occurrence of the state of dispersions, from stable to unstable, or vice-versa is important in many non-engineering applications as well, for example in food industries at large level, in medicinal field, in water purification, paints and cosmetics etc. [19].

The colloidal stability is controlled by the interactions between the particles, mainly through electrostatic or steric phenomena. Ionic strength, ion valence and pH could make a significant impact on colloid stability. In this study, the main focus was on investigating the effect of pH to the colloid stability which can be achieved through changes in HNO₃ and/or NaOH concentrations in the colloidal solution. Fig. 3 shows the variation of colloid stability for high-endemic and low-endemic soil colloids respectively, with the different pH conditions in the solution.

High-endemic soil colloids showed lower overall stability compared to the low-endemic soil, suggesting that high-endemic soil colloids are



(a)



(b)

Fig. 3. Colloid stability tests for (a) High-endemic soil (b) Low-endemic soil

more transportable and mobile in subsurface environments. Moreover, both soil colloids were more unstable in acidic environments when compared to the basic pH conditions. This could be due to the increment of negative charge on the colloidal particles and thereby the increment of surface potential with the increasing pH conditions [20, 21, 22]. Also, at higher pH values soil colloids exhibited higher stability against coagulation/flocculation due to increased electrostatic repulsion. Further, Na⁺ and OH⁻ ions in the solution is also increasing leading to more repulsion between ions and the negatively-charged colloids [23]. Furthermore, when pH is increasing, the positive ions in the solution is decreasing (i. e. negative ions in the solution is increasing). Since the colloidal particles are also negatively charged they repel each other due to the presence of these identical and equivalent charges and do not join together to form larger particles that hold them scattered in the medium and stabilize the colloidal remains. Therefore, they will remain as a suspension and hence stable against coagulation/flocculation [24].

CONCLUSIONS

Regardless of the similarity between the physico-chemical of two soil samples, a significant difference was observed in the stability of water dispersible colloids extracted from the two soils with varying pH. The developed numerical model could adequately describe the observed colloid turbidity with time with the optimized model parameter (t^*).

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