



The influence of Na^+ and Ca^{2+} on the migration of colloids or/and ammonia nitrogen in an unsaturated zone medium



HaiMing Li ^{*}, JinBu Wei, YaChao Ge, ZhanQuan Wang, Ye Wang, YingLong Li

^a Laboratory of Coastal Groundwater Utilization & Protection, Tianjin University of Science & Technology, Tianjin 300457, China

^b Tianjin Marine Resources and Key Laboratory of Chemical, Tianjin 300457, China

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ABSTRACT

This experiment was conducted with an indoor sand-column device, the migration of colloids with the presence of Na^+ and Ca^{2+} and the migration of ammonia nitrogen with the presence of Na^+ , Ca^{2+} or/and colloids was studied. The results showed that the migration of colloids was influenced by the ion valence state, different ions with different valence could block the migration of colloids. In addition, the blocking effect of bivalent ions was more obvious than that of monovalent ions. In the presence of Na^+ and Ca^{2+} , the R_d value of the ammonia-nitrogen migration process were 1.01 and 1.41, respectively, which indicated that bivalent ions have a greater blocking effect on ammonia-nitrogen migration than monovalent ions. Colloids could also block the ammonia-nitrogen migration, and R_d value in the ammonia-nitrogen migration process was 1.17. Moreover, the presence of Na^+ /colloids and Ca^{2+} /colloids could enhance the blocking effect on the ammonia-nitrogen migration, and resulting the R_d values at 1.20 and 1.52, respectively. The cohesion of colloids caused by the compaction of its electric double layer with those ions added maybe the key causes of those blocking.

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1. Introduction

Ammonia nitrogen is widely detected in groundwater. The ammonia-nitrogen concentration in groundwater in some wells in southern Iowa in the United States of America (USA) is over 0.78 mg/L (Schilling and Jacobson, 2008). In the northwest Europe, the maximum ammonia-nitrogen concentration found in a group of 80 wells is 1.4 mg/L, which is significantly beyond the groundwater quality standard (Andres and Enn, 2008). In China, the maximum ammonia-nitrogen concentrations found in groundwater in Qiqihaer and Shijiazhuang are 0.80 and 1.11 mg/L, respectively (Liu et al., 2001). The proportion of ammonia nitrogen pollution is increasing, and the geographical scope of ammonia nitrogen pollution is continually expanding (Chen, 2011). Infiltration into soil or groundwater is an important water-circulation process of surface water (precipitation, irrigation water, rivers, etc.), and this is the main way that ammonia nitrogen gets into the groundwater environment (Feng and Huang, 1997; Yang et al., 2007; Wen et al., 2004).

As ammonia nitrogen infiltrates into soil, it will be adsorbed onto the vadose soil and colloids particles (Chen, 2011). Colloids is a decentralized system, and the dispersed phase particle diameter is about 10^{-9} – 10^{-7} m. Because of the huge specific surface area and surface charge, colloids has high adsorption energy, and showing a greater

affinity for pollutants (Bake and Pitt, 1996; Barton and Karathanasis, 2003; Ryan and Elimelech, 1996). There are plentiful colloids in natural water-bearing media. Coastal vadose soil contains much Na^+ , Ca^{2+} and colloids, and the content of colloids increases as surface water infiltrates into groundwater, and increasing the migration ability of sorbed pollutants (Citeau et al., 2003; Crancon et al., 2010; Denaix et al., 2001; Li et al., 2013; Sen and Khilar, 2006). Meanwhile, Na^+ , Ca^{2+} in the unsaturated zone and surface water could also affect the migration ability and speed of colloids, and thus further affect the migration ability of pollutants.

The chemical composition of the water phase and the migration-deposition characteristics of colloids in the aquifer medium are strongly related. Changing of the ions valence and ions concentration in aqueous solution (monovalent and bivalent ions) could cause the changing of the colloids nature (Amy, 2001). Daniel and Michal (2006) compared the effects of monovalent (Na^+) and bivalent (Ca^{2+}) cations on colloids deposition, and found that the concentration of colloids is reduced with the increasing ion concentration. With Na^+ added, the largest colloids concentrations are over 10 mg/L, but these values for Ca^{2+} are <0.1 mg/L. At the same time, they analyzed the migration behavior of colloids in a saturated sand column, and found that the main mechanism of colloids migration is convection dispersion and deposition. Liu and Elimelech (1995) found that the ionic strength of the solution influences the dynamics of colloidal deposition and transportation in heterogeneous porous media by controlling the range and magnitude of interparticle forces. Roy and Dzombak (1996) found that reducing the ionic strength can promote the releasing of colloids. When the concentration of Na^+ decreases from 0.05 to 0.001 mol/L, the maximum

^{*} Corresponding author at: College of Marine and Environmental Sciences, Tianjin University of Science & Technology, Tianjin 300457, PR China.
E-mail address: lhm@tust.edu.cn (H. Li).

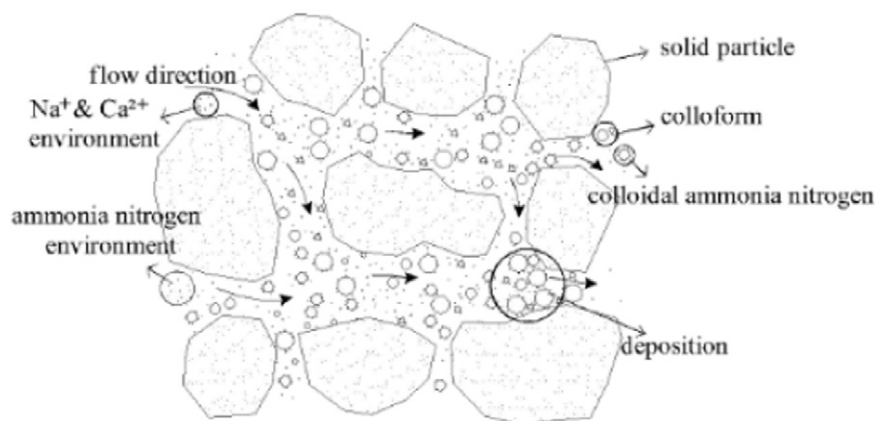


Fig. 1. Migration of ammonia nitrogen and colloids in water-bearing Media.

concentration of released colloids increases from 64 to 12,500 mg/L. This is because higher ionic strength leads to higher energy barriers, and release rate coefficients are exponentially affected by the energy barrier values. The rate and total mass of colloids release are also increasing quickly with the greater reduction of ionic strength. To discuss the functions of colloids generation and transport, Seaman et al. (Seaman et al., 1995) found that increasing the value of SAR (sodium adsorption ratio) would decrease the turbidity of effluent water from 18 to 4.5 NTU. The degree of colloids generation decreased with the increasing Na^+ concentration and the prolonged exposure duration in the high SAR solutions. Additionally, as the Ca^{2+} concentration increased from 0.001 to 0.01 mol/L, the turbidity of the effluent water samples decreased from 8 to 6.5 NTU, indicating that ionic strength make critical impact on colloids formation and migration. Corapcioglu and Jiang (1993) reported that the capture and adsorption of the colloids could obviously influence the migration behavior of solution. Chung and Zasoski (1994) found that in the rhizosphere samples, selectivity for NH_4^+ over K^+ is relatively higher at an ionic strength of 0.02, but reversed when ionic strength reach to 0.05. Some other studies also show that the content of other cations has an effect on ammonia-nitrogen adsorption in the unsaturated zone (Lumbanraja and Evangelou, 1994; Shen et al., 1997). But only few studies have addressed the influence of Na^+ and Ca^{2+} in aqueous solution on the migration of colloids and colloid-adsorbing ammonia nitrogen at the same time.

In this study, the migration characteristics of ammonia nitrogen were studied in the Na^+ and Ca^{2+} system in aqueous solution. In the ammonia nitrogen migration process in water-bearing media, ammonia nitrogen could adsorb on the surface of colloids when colloids exists. This ammonia nitrogen is called colloidal ammonia nitrogen. In the Na^+ and Ca^{2+} system in aqueous solution, the deposition of colloids will lead to the deposition of ammonia nitrogen adsorbed on the colloids surface, and the migration of ammonia nitrogen and colloids in the water-bearing media is shown in Fig. 1. An indoor sand column experiment was conducted to focus on the influence of ions with different valences on the migration of colloids or/and ammonia nitrogen, which is helpful in revealing the migration characteristics and mechanism of ammonia nitrogen in the groundwater system.

2. Materials and methods

2.1. Preparation of colloids

Natural clay 100 g was collected from the field sediments in Tianjin, China, then screened through a 60-mesh sieve and put into a 1000 mL beaker. In order to avoid changing the natural properties and stability of the colloids, 1000 mL deionized water was added into the beaker, stirred and shaken for 30 min with ultrasonic dispersion to separate the colloids from the surface of solid particles quickly. After 24 h settling,

the colloids suspension was obtained when the colloids contained was enough to sediment, flocculate or aggregate (Luo, 2009). In order to separate of colloidal particles from those suspension, the suspension was filtered through a 0.8 μm membrane filter to obtain the colloidal stock solution (Zheng and Qian, 1998a). The colloids used in this experiment was all from the colloidal stock solution.

2.2. Nature of the colloids

2.2.1. Colloids concentration

The concentration of colloids was measured by the turbidity method. According to the correlation between standard colloids concentration and their turbidity, a standard calibration curve was obtained (Fig. 2). The colloids concentration of the solution could be calculated by its turbidity.

2.2.2. Particle size

A Malvern Zeta-sizer Nano-ZS90 produced by Malvern Instruments Ltd. (Worcestershire, United Kingdom) was employed to measure particle size of colloids. The measurement range is 1 nm–3 μm . The particle size distribution is normal distribution. The monodisperse sample accuracy is 2%. The repeatability is $\pm 2\%$. The light source is a 633 nm red laser. The temperature is controlled at 25 $^\circ\text{C}$. Solution samples 1–1.5 mL was used and the measured average particle size of colloids in this experiment is 315 nm.

2.2.3. Zeta potential

A Malvern Zeta-sizer Nano-ZS90 was used to measure zeta potential of colloids. The particle size ranges between 5 nm to 10 μm . The zeta

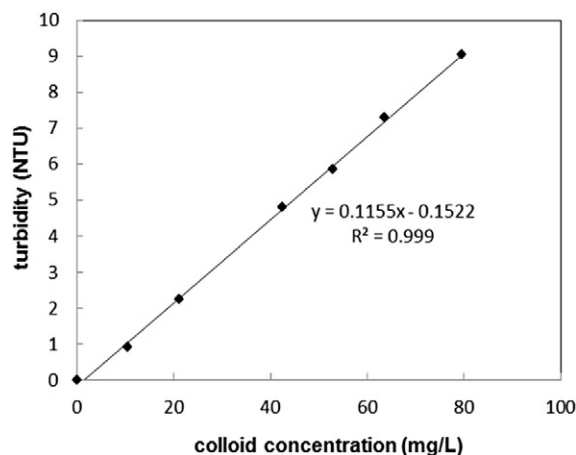


Fig. 2. Calibration curve of standard colloids concentration and their turbidity.

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