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Adsorption and transformation of ammonium ion in a loose-pore geothermal reservoir: Batch and column experiments

Li Zhao [a,b,*], Yanli Li [a], Shidong Wang [c], Xinyi Wang [a], Hongqi Meng [a], Shaohe Luo [a]

[a] Institute of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China
[b] Collaborative Innovation Center of Coalbed Methane and Shale Gas for Central Plains Economic Region, Henan Province, Jiaozuo 454000, China
[c] Xi'an Research Institute of China Coal Technology & Engineering group, Xi'an 710054, China

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ABSTRACT

Adsorption kinetics and transformation process of ammonium ion (NH_4^+) were investigated to advance the understanding of N cycle in a low-temperature loose-pore geothermal reservoir. Firstly, batch experiments were performed in order to determine the sorption capacity and the kinetic mechanism of NH_4^+ onto a loose-pore geothermal reservoir matrix. Then column experiments were carried out at temperatures from 20 °C to 60 °C in order to determine the transport parameters and transformation mechanism of NH_4^+ in the studied matrix. The results showed that the adsorption process of NH_4^+ onto the porous media well followed the pseudo-second-order model. No obvious variation of hydrodynamic dispersion coefficient (D) and retardation factor (R) was observed at different transport distances at a Darcy's flux of 2.27 cm/h, at which nitrification could be neglected. The simulated D obtained by the CDE model in CXTFIT2.1 increased with temperature while R decreased with temperature, indicating that the adsorption capacity of NH_4^+ onto the matrix decreased with the increasing of temperature. When the Darcy's flux was decreased to 0.014 cm/h, only a little part of NH_4^+ could be transformed to nitrate, suggesting that low density of nitrifiers existed in the simulated loose-pore geothermal reservoir. Although nitrification rate increased with temperature in the range of 20 °C to 60 °C, it was extremely low and no accumulation of nitrite was observed under the simulated low-temperature geothermal conditions without addition of biomass and oxygen.

1. Introduction

With the excessive exploitation of low-temperature geothermal water with a temperature varying from 35 °C to 68 °C in the North China Plain, many hydro-geological and environmental problems have occurred over the last few years. For example, the water table in the 1000–1200 m stratum in Kaifeng City, Henan province, China dropped from 17 m to 66.07 m after 13 years of overextraction (Wang et al., 2013). In addition to the drop of water table, NO_2^--N and NH_4^+-N concentrations of geothermal water, exploited from a loose-pore geothermal reservoir which is composed of the Minghuazhen Formation in the Neogene Period with a depth between 600 m and 1400 m, elevated quickly. The phenomena indicated the occurrence of denitrification, which was probably induced by the alteration of the microbial environment and the redox conditions (Zhao et al., 2014). When used for drinking, high NH_4^+ content in geothermal water might reduce disinfection-efficiency and cause problems in senses of smell and taste (World Health Organization, 1993). And nitrite in the intestine may cause methemoglobinemia and form carcinogenic compounds such as nitrosoamines in the stomach (Gómez et al., 2000; Kapoor and Viraraghavan, 1997).

* Corresponding author at: Institute of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China.
E-mail address: zhaoli@hpu.edu.cn (L. Zhao).

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Influencing factors of adsorption, equilibrium isotherms of ammonium ion onto the loose-pore reservoir and transport mechanism have been investigated in our previous studies (Wang et al., 2013; Zhao et al., 2011). Moreover, the transformation and transport mechanism of nitrate ion through the same matrix have also been discussed through column experiments (Wang et al., 2013). However, the nitrogen cycle in the geothermal water was still not fully understood. There is a need to investigate adsorption kinetics of ammonium ion onto the studied matrix as well as the transformation mechanism of ammonium ion in the studied area.

Biological transformation of ammonium ion has been widely studied in wastewater, soil, coal, wetlands, sea water, river and groundwater, etc. The transformation process includes autotrophic and heterotrophic nitrification. While heterotrophic nitrification generally occurs under a low pH condition (De and Kowalchuk, 2001; Ge et al., 2015; Gutierrez-Zamora et al., 2015; Miller and Smith, 2009), the autotrophic aerobic nitrification of ammonium ion is a two-step process, carried out by two categories of chemolithotrophic microorganisms: ammonia-oxidizing bacteria (AOB) or archaea (AOA), and nitrite-oxidizing bacteria (NOB). In both steps oxygen is the electron acceptor (Niu et al., 2013). The process can be described by the following equation (Campos et al., 1999):

$$NH_4{}^+ + 1.86O_2 + 1.98HCO_3^- \rightarrow 0.02C_5H_7O_2N + 0.98NO_3^- + 1.88H_2CO_3 + 1.04H_2O \quad (1)$$

where $C_5H_7O_2N$ represents the chemical composition of the bacterial cell of *Nitrosomonas* and *Nitrobacter*.

This equation indicates that bicarbonate is used as a carbon source for autotrophic microorganisms. According to previous reports, the process can be affected by various factors, such as temperature, pH, dissolved oxygen (DO), salinity, moisture, ammonia and nitrite concentrations, carbon to nitrogen ratio, and hydraulic retention time (HRT), etc. (Chen et al., 2006; Chen et al., 2015; Fitzgerald et al., 2015; Lee et al., 2014; Lei et al., 2007; Liu and Wang, 2015; Ste-Marie and Pare, 1999; Sudarno et al., 2011; Wu et al., 2014; Yamaguchi et al., 1996; Yusof et al., 2010). Partial nitrification is usually achieved by providing growth conditions including high temperature, high pH, low DO concentration, high free ammonia concentration or addition of chemicals for inhibition of nitrification, which are favorable for AOB but inhibits NOB growth (Daverey et al., 2012; Ge et al., 2015; Gu et al., 2012; He et al., 2012; Wu et al., 2014). Under low DO, the growth rate of NOB is much lower than AOB, therefore nitrite accumulation occurs (Daverey et al., 2012; Wu et al., 2014). In addition to autotrophic bacteria, a wide phylogenetic range of heterotrophic bacteria and fungi can carry out nitrification, particularly in acid soils where autotrophs are inhibited by low pH (De and Kowalchuk, 2001). And some studies suggested that unidentified organic N compounds could also be used as substrates for heterotrophic nitrification (Barraclough and Puri, 1995). However, little is known about the biological transformation of ammonium ion and its influential factors on nitrification process in underground pore water at depths below 600 m.

The objectives of the present work are: (1) to study the adsorption kinetics of ammonium ion onto loose-pore geothermal reservoir matrix through batch experiments; (2) to evaluate the transport and adsorption parameters of ammonium ion at different transport distances in a simulated loose-pore and low-temperature geothermal reservoir through column experiments and numerical simulations; (3) to investigate the transformation process of ammonium ion at different transport distances and quantify the impact of temperature on nitrification under the simulated geothermal environment.

2. Materials and methods

2.1. Batch experiments methodology

The loose-pore geothermal reservoir matrix used for the tests was obtained from a geothermal reservoir which is composed of Minghuazhen Formation in Neogene Period with a depth between 600 and 1400 m, bared from 60 m deep valley in Wang-Gou village, Qu-Liang town, Xin-Mi country, China (Wang et al., 2013). Before use, all samples were air dried and ground to pass through a 2 mm screen.

Batch studies were conducted in a temperature-controlled shaker using 50 mL of aqueous solution with 5.0 g loose-pore geothermal reservoir matrix. The agitation speed of the shaker was fixed at 150 rpm for all batch experiments. The experimental temperature varied from 20 to 60 °C. The samples collected at different time intervals (1 min, 5 min, 15 min, 30 min, 60 min,120 min and 180 min) were filtered through a 0.45 μm filter membrane. The obtained filtrates were analyzed by the conventional Nesslerization method to determine the NH_4^+ ion concentration remaining in the aqueous solution (State Environmental Protection Administration of China, 1987).

In order to test the possibility of any adsorption on the walls of the glass conical flask, control experiments were carried out with NH_4^+ ion solution in the absence of studied matrix. It was observed that there was no adsorption by the container wall. All the experiments were performed in duplicate and mean values were presented with a maximum deviation of 5%.

2.2. Column experiments methodology

Two acrylic columns (0.16 m I.D. and 0.85 m Height) were filled with 23.46 kg of well-mixed matrix. The setup is shown in Fig. 1. The structure of the column and the method of packing of air-dried matrix were similar to those used in previous studies (Wang et al., 2013; Zhao et al., 2014). The columns were placed in identical incubators under darkness as described previously (Wang et al., 2013) and run at different temperatures. Each column contained 2 sampling ports. The first port was positioned exactly at the center of the top of the column (85 cm), while the other was located at 45 cm from the base. At each sampling port, a 0.5 cm I.D. tube was extended from the top of the column or from the column wall to the center of the column. To prevent sediment from entering the sampling port, a piece of nylon mesh was placed in the inner end of the tube. A peristaltic pump was used for the delivery of infiltration solutions containing 50 mg/L NH_4^+-N prepared by diluting the NH_4Cl stock solutions with deionized water in an upward direction.

Although Wang et al. (2013) have studied ammonium ion transport and adsorption mechanisms at an average Darcy's