Adsorption Kinetics of Ammonium Ion onto Unconsolidated Geothermal Reservoir Medium

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Abstract The frequent exploitation of geothermal resources can induce the oxidation of ammonium ion to nitrite. To explore the NH_4^+ ion transport processes in unconsolidated geothermal reservoir medium, the adsorption kinetics of NH_4^+ ions from aqueous solutions onto unconsolidated geothermal reservoir medium were studied through batch experiments. The results indicate that the adsorption of NH_4^+ ion is a spontaneous, exothermic process and the adsorption is higher at lower temperatures. Kinetic analysis at different temperatures shows that the adsorption of NH_4^+ ion onto sediment from unconsolidated geothermal reservoir well follows the pseudo-second-order model, indicated by the regression coefficient($R^2=1$).
Keywords ammonium, adsorption, kinetics, fine sand

Introduction

A large quantity of geothermal water has been exploited from unconsolidated geothermal reservoir in the North China Plain, and the quantity of exploited deep geothermal water including mine water has been increasing over the years. The geothermal exploitation activities have caused some engineering and environmental problems including dropping in well water levels and fast increase in nitrite concentration in the geothermal water over the last years (Zhao et al. 2014).

As the extent of geothermal water exploitation is increasing quickly, the NH_4^+ ion may be easily oxidized to NO_2^- with more oxygen dissolved in geothermal water. Furthermore, the geothermal water may be polluted by nitrogenous compounds from terrestrial or shallow groundwater and more NH_4^+ ion may be oxidized. Nitrite, as an intermediate in nitrification and denitrification reactions, is highly toxic to plants, animals and humans (Lewis and Morris, 1986). Some reports indicate that NO_2^- can accumulate in ecosystems (Shen et al. 2003). In order to explore the NH_4^+ ion movement in unconsolidated geothermal reservoir medium, it is necessary to firstly study the kinetic adsorption of ammonium onto unconsolidated geothermal reservoir medium.

Materials and methods

Materials

The sediment used was fine sand derived from geothermal reservoir which was composed of Minghuazhen Formation in Neogene period, bared from 50m-deep valley in WangGou village, QuLiang countryside, XinMi county, China(Wang et al., 2013)**.** Before use, all samples were air-dried and ground to pass through a 2-mm screen. The total organic carbon (TOC) and cationic exchange capacity (CEC) were 0.0745% and 22.41 cmol/kg respectively.

Ammonium chloride salt (Guaranteed reagent grade, purity $\geq$99.8%) and deionized water were used for the preparation of a stock NH_4^+ solution of 1000mg/L. Ammonium solutions of different concentrations were prepared by diluting the NH_4Cl stock solution with deionized water.

Experimental methods

Batch studies were conducted in a temperature-controlled shaker using 50 mL of aqueous solution with 5.0 g sediment. The agitation speed of the shaker was fixed at 150 rpm for all batch experiments. Since the ammonium adsorption onto the studied matrix is spontaneous and belongs to physisorption process at all studied conditions, the experiments were not carried out under inert gas atmosphere. The experimental temperature varied from 20 to 60 ℃. 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 (SEPA 2002).

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 sediment. 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%.

Results and discussion

The effect of contact time on ammonium adsorption

Several experiments were carried out to study the effect of contact time on NH_4^+ ion adsorption on the studied sediment. 50mL of NH_4^+ solution (50 mg/L) and 5 g of sediment were mixed and shaken at certain temperature(20 ℃，40 ℃，60 ℃ respectively) for different contact period ranging from 1 to 180 min. The results (Figure1) indicate that the adsorption is higher at lower temperatures. So the adsorption of NH_4^+ ion onto sediment is a spontaneous, exothermic process. This result is consistent with the results in literature (Zhang and Sun 2009). Moreover, the adsorption of NH_4^+ ion onto sediment was fast with over 60% of the initial NH_4^+ ion in solutions being achieved within the first 15 min and then reached equilibrium state for the three temperatures. This behavior may be attributed to the quick utilization of the most readily available adsorbing sites of the sediment leading to fast diffusion of NH_4^+ ion and attainment of rapid adsorption equilibrium(Karadag et al. 2006). After approximately 1h of adsorption, sorption equilibrium begins to establish itself at 20 ℃，40 ℃ and 60 ℃. On the basis of these results and analysis, a 60min contact period was selected for subsequent studies.
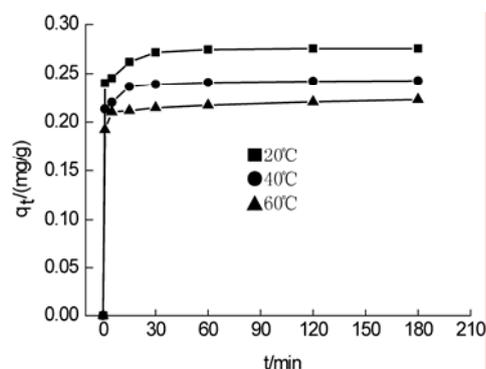

Fig. 1 *Effect of contact time on adsorption amount at different temperature (initial NH_4^+ ion concentration=50mg/L, sediment /solution=5g/50mL).*

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To study the adsorption mechanism of NH_4^+ ion uptake onto the sediment, the pseudo-second-order kinetic model and the intra-particle model were used; the kinetic equation of the pseudo-second-order is as follows(Lei et al. 2008):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(1)

Where the k_2 is the rate constant of pseudo-second-order model(g/(min·mg)), q_t and q_e are the amounts of NH_4^+ ion adsorbed onto sediment at time t and at equilibrium(mg/g), respectively.The values of k_2 and q_e can be calculated from the slope and the intercept of the straight-line plots of t/q_t versus t are noted in table1. The plots of the pseudo-second-order kinetic at different temperatures are shown in Figure 2. As seen from Table 1 and Fig. 2, the good correlation coefficients($R=1$) confirm that the adsorption of NH_4^+ ion on sediment can well follow the pseudo-second-order model.
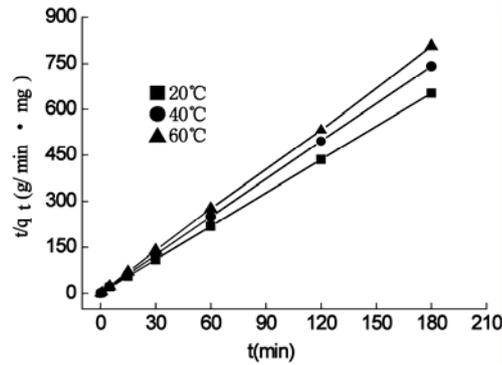

Fig. 2 Pseudo-second-order kinetic model for NH_4^+ adsorption onto sediment at different temperatures.

Table 1 Rate constants and correlations coefficients for the studied kinetic models

Temperature (℃)	Pseudo-second-order model			Intra-particle diffusion model	
	k_2(g/min mg)	q_e(mg/g)	R^2	k_1(mg/(min$^{1/2}$g))	R^2
20	9.0844	0.276	1.00	0.00282	0.728
40	8.303	0.242	1.00	0.00211	0.671
60	7.5702	0.2242	1.00	0.00187	0.712

The intra-particle diffusion is represented by:

$$q_t = k_1 t^{1/2} + C$$

(2)

Where k_1 is the intra-particle diffusion rate constant(mg/(min$^{1/2}$ g)), q_t is the amount of NH_4^+ adsorbed at the time of t(mg/g), and C is the intercept （Karadag et al. 2006）. The values of k_1 and correlation coefficients are given in Table1. As seen from table 1, the low correlation coefficients($R^2<0.75$) obtained confirm that the intra-particle diffusion model can not be well applied to describe NH_4^+ ion adsorption on sediment. These results suggest that NH_4^+ adsorption onto geothermal reservoir fine sand involves only one stage:surface sorption based on the assumption that the rate limiting step might be chemical adsorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate.

Conclusions

Based on the experimental and simulation results obtained under the conditions of fine sand with low clays contents derived from geothermal reservoir that was composed of

Minghuazhen Formation in Neogene period, it can be concluded that it is favored for the adsorption of NH_4^+ ion from aqueous solutions. But the adsorption capacity is lower than other absorbents such as zeolite, sepiolite, montmorillonite and clay. The adsorption of NH_4^+ ion onto the matrix is a spontaneous, exothermic process and the adsorption is higher at lower temperatures. Between the two rate kinetic equations, the pseudo-second-order kinetic model agreed better with the dynamical data of the adsorption of NH_4^+ ion onto geothermal reservoir. Intra-particle diffusion model was also applied to this system with R^2 values varying from 0.671 to 0.728 with the rise in temperature from 20 ℃ to 60 ℃.

Acknowledgements

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