SOIL CHEMISTRY

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KINETIC ADSORPTION OF AMMONIUM ONTO SOME LOESS SOILS OF NORTHERN IRAN

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Abstract. The study of adsorption kinetics is very useful for understanding the mechanisms that are involved. In order to predict the mechanism involved during the present sorption process and the potential rate controlling steps such as mass transport, pore diffusion and chemical reaction processes, several kinetic models were used to fit the experimental data, namely, zero-order, first-order, pseudo-second-order, simplified Elovich, parabolic diffusion and power function models. At the present study, an ammonium adsorption kinetic experiment was conducted using solution containing 100 mg/l of ammonium chloride at the times of 0.25 to 384 h. Kinetic equations for ammonium adsorption were evaluated by comparing coefficients of determination (r^2) and standard errors of estimate (SE) for each equation, which were determined by least square regression analysis. The results of adsorption kinetic study showed that ammonium is adsorbed fast within the first hours, but with elapsing the time, it will be slow. The most ammonium adsorption was in Kordkoy soil and the lowest one was observed in the Houttan soil 2. The rates of ammonium adsorption in all soils could be best described by the pseudo second order, power function and simplified Elovich equations.

Key words: Adsorption, ammonium, kinetic.

INTRODUCTION

Nitrogen is an essential macronutrient for plant and in the modern agriculture, nitrogen deficiency is very common. Ammonium and nitrate are important inorganic forms of nitrogen in soil. Ammonium can be fixed among layers of some 2:1 clay minerals, particularly vermiculite and Illite (Hadas etal., 1986). The fixed ammonium and ammonium-fixing capacity is positively correlated with the amount of 2:1 type clay minerals (Zhang, 2006).

Understanding the kinetics and reaction mechanism involved is essential for fully understanding the dynamic interactions of nutrients with soil and predicting their fate over time, dynamic, species formation and bioavailability of nutrients (Sparks, 1989 and 2000). Adsorption can be known as the accumulation of substance or material at interface between solid surface and surrounding solution. Adsorption and desorption are time-dependent processes, and knowledge of adsorption and desorption rates are essential for planning, evaluation and recovery of adsorbent. Ammonium adsorption kinetic was investigated by many researchers and various kinetic models were used to fit the data. Various kinetic models like zero, first and pseudo-second orders, power function, simple Elovich and parabolic diffusion models were used to describe the kinetic of soil chemical processes such as ammonium adsorption kinetic (Sparks, 1986).

Zhu et al (2011), in the study of Kinetic adsorption of ammonium nitrogen by various substrate materials reported that ammonium adsorption by different materials initially rises sharply, after a while it becomes slow, and finally reaches a constant level. They also stated that pseudo-second order equation is the best model to explain the ammonium adsorption. Kithome et al (1998) in the study of ammonium adsorption and desorption kinetics by natural zeolite clinoptilotite reported that the adsorption process reaches equilibrium at 60 to 120 minutes. They introduced the first order, Elovich, parabolic diffusion and homogeneous diffusion equations as the best describing equation of ammonium adsorption. Lebedynets et al (2004) also investigated the adsorption of ammonium on natural zeolite and concluded that ammonium adsorption reaches equilibrium in 24 h and then it becomes constant. They introduced the first-order equation as the best model to explain the adsorption of ammonium. The aim of this research was to investigate the adsorption of ammonium in some loess derived soils in the north of Iran, and to select the best describing equation of ammonium adsorption kinetics.

MATERIAL AND METHODS

Soil samples from the areas in Kordkouy, Houtan and the Karasu in the north of Iran, Golestan province were collected, air-dried and passed through a 2 mm sieve. Soil texture (Gee and Bauder, 1986), calcium carbonate (Nelson, 1982), organic carbon (Nelson and Sommers, 1982), pH and electrical conductivity (Rowell, 1995) and CEC (Chapman, 1965) of soil samples were determined. Kinetic experiments were performed using batch technique (Zhu et al, 2011). In this method, 2 g soil samples in triplication were weighed and poured into centrifuge tube. Then, 2 ml ammonium chloride solution (100 mg/l) was added and shaken for 2, 4, 8, 16, 24, 48, 96, 192, and 384 h time intervals (Steffens and Sparks, 1997). After shaking, each sample was centrifuged at 3000 rpm for 5 minutes, and then equilibrated ammonium concentration in the supernatant was determined using Steam distillation apparatus. The adsorbed ammonium content was obtained from the difference of initial and equilibrium ammonium concentrations in the solution. Two drops of chloroform were added to each sample to inhibit microbial activities at the beginning of experiment. Six kinetic models i.e. zero-order, first-order, pseudo-second-order, simplified Elovich, parabolic diffusion and power function, were used to fit the experimental data. Kinetic equations for ammonium adsorption were evaluated by comparing coefficients of determination (r^2) and standard errors of estimate (SE) for each equation, which were determined by least square regression analysis.

RESULTS AND DISCUSSION

Some physical and chemical properties of the soils are given in Table 1. The selected soils had different clay content and minerals. Smectite was dominant in the soils collected from Kordkoy and Karasou, while illite was prevailing in the soils of Hottan (Farshadirad et al, 2012; Bahreini et al, 2010).

Table 1 - Some physical and chemical properties of the soils

			Clay	CCE	OM	CEC
Soils	Texture	pH		%		Cmol(+)/kg
Houtan 2	SiL	7.2	11	13	0.5	13.5
Karasou	C	7.3	48	26	2.8	23.7
Kordkouy 1	SiC	7.5	28	2	2.7	26.7

Ammonium adsorption of soils

Ammonium adsorption in soils as a function of time is shown in Fig 1. In initial stages, ammonium is rapidly adsorbed with soil. But with time, the curve slope and the ammonia adsorption are reduced. The adsorption capacities of the all soils increased steeply from 0 to 8 h, then rose progressively from 8 to 24 h, and finally reached equilibrium after 24 h. This can be explained with the availability of adsorbent sites at early-stage of adsorption and with the saturation by ammonium by the passing of time. Zhu et al (2011) also found similar results. When the adsorption sites were occupied, the adsorption rate declined and became equal to the desorption rate at the end. The biphasic adsorption or release (initial rapid and the next slow phases) is the characteristic of a process that is controlled by diffusion, which has been previously observed for ammonium (Steffens and Sparks, 1997; Kithome et al, 1998), and other similar ions such as potassium

(Feigenbaum et al, 1981); Martin and Sparks, 1983). Ugurlu and Karaoglu (2011) concluded that ammonium adsorption with fly ash and sepiolite reaches equilibrium in nearly 1 h, afterwards, adsorption rate fixes. Kithome et al (1998) reported that ammonium adsorption by natural zeolite clinoptilolite reaches equilibrium at 60 to 120 min. Liu et al (2010) stated that the ammonium adsorption process from aqueous solution by strawberry leaf powder occurs in three steps. The ammonium adsorption occurred slowly and steadily in the initial stage. The adsorption capacities increased sharply within the middle stage, and the adsorption processes reached equilibrium in 14 h. The equilibrium might be due to the saturation of the efficient active sites.

Among soils, Kordkouy had the most ammonium adsorption, and Houtan 2 had the lowest. Higher adsorption in Kordkouy soil can be attributed to its high percentage and type of clay. Ammonium adsorption has also increased with the increase of clay content. The adsorption of ammonium in soils with dominant smectite was more than Illite dominant soils. Karasou soil adsorption was less than Kordkouy-1 soil. Because Karasou soil has a high lime (table 1), it probably masked the adsorbent sites and the ammonium adsorption was prevented. Steffens and Sparks (1997) stated that non-exchangeable ammonium release from soils reduced with acidic resins. This is due to neutralization with lime.

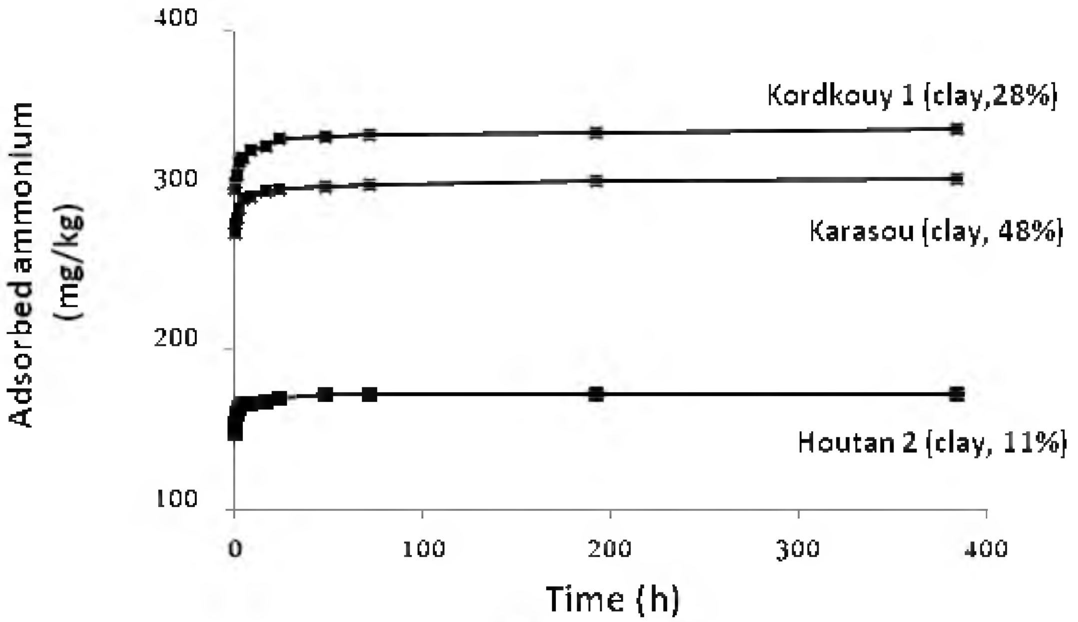

Figure 1 - Adsorption of soils from ammonium chloride solution

Comparison of kinetic equations

Standard error of estimate (SE) and coefficients of determination (r^2) for the different fitted equations in different soils are presented in Table 2. Mathematical analysis of the ammonium adsorption data showed that pseudo-second order, power function and simplified Elovich equations were the best model to describe the ammonium adsorption rate by the soils. Pseudo-second-order and power function equations fitted on the data of ammonium adsorption by soils are shown in figures. 2 and 3. Lagergren pseudo-second-order model was widely used to estimate the ammonium adsorption kinetics (Ho and Mckay, 1994). Researchers found that if a reaction is controlled by ion exchange, the pseudo-second order model has best fit with the experimental data (Lei et al., 2008); Zheng et al., 2008). Pseudo-second-order equation was introduced by Ugurlu and Karaoglu

(2011) and Moussavi et al (2011) as the best model to explain the adsorption of ammonium by fly ash, sepiolite and natural zeolite. Zhu et al. (2011); Huang et al. (2010); Wahab et al. (2010); Liu et al. (2010); Guo et al. (2008) and Wen et al. (2006) also reported that the pseudo-second order equation is the best model to explain the ammonium adsorption.

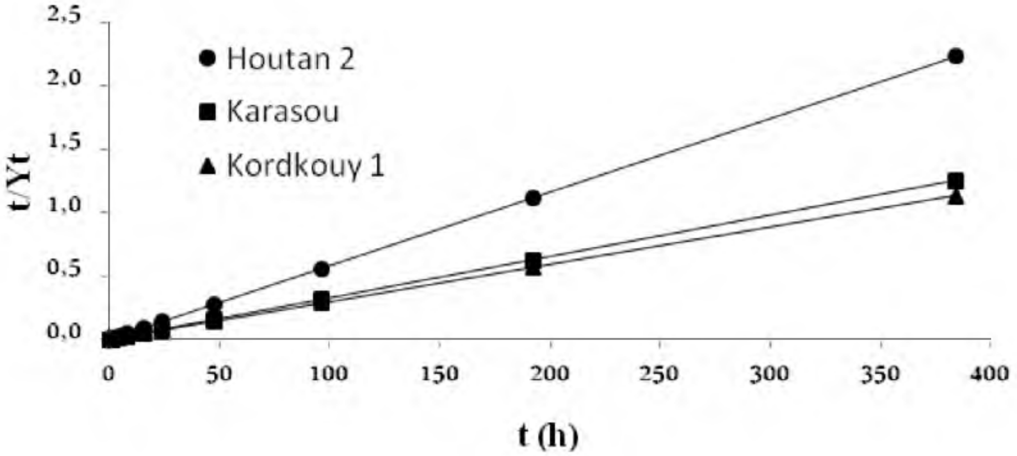

Figure 2 - Kinetic of ammonium adsorption according to Pseudo-second-order model for the soils

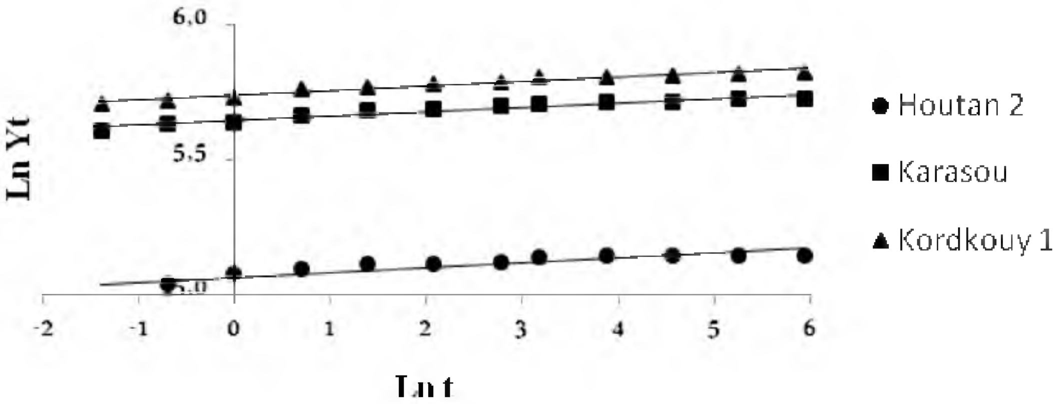

Figure 3 - Kinetic of ammonium adsorption according to power function model for the soils

Table 2 - Standard error of estimate (SE) and coefficients of determination (r^2) for adsorption kinetic equations on the soils

	Simplified Elovich		Power function		Pseudo-second-order		First-order		Zero-order		Parabolic diffusion	
Soils	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2
Houtan 2	3.28	0.84	0.02	0.84	0.0018	1	0.38	0.80	5.54	0.52	5.92	0.47
Karasou	2.97	0.94	0.01	0.93	0.006	1	0.47	0.81	8.87	0.41	7.46	0.59
Kordkouy 1	3.09	0.95	0.01	0.94	0.003	1	0.53	0.73	10.02	0.42	8.31	0.61

The good fit of the power function and simplified Elovich models to ammonium adsorption data indicate a slow diffusion of ammonium into interlayer position of the soil minerals and rate controlling process. Kinetic studies performed on potassium which behaves very similar to ammonium (Sparks and Huang, 1985) suggest that parameters similarity of three well fitted models of simplified Elovich, power function and parabolic diffusion is indicative of slow potassium diffusion from/into interlayer positions of mica and rate controlling process. Bache and Williams (1971) indicated that the energy of adsorption decreased exponentially with the increase of surface saturation when the adsorption fitted the Freundlich equation or power function (Kuo and Lotse 1974).

Interactions between the molecules may explain the decreasing energy of adsorption with surface saturation increase.

CONCLUSION

The results showed that in all studied soils, ammonium adsorption pattern was as a rapid response that lasted about 8 h which continued by a slower reaction and finally reached equilibrium in 24 h. Among the soils, the most ammonium adsorption was in Kordkoy soil and the lowest one was in the Houttan soil 2. Comparison of Standard error of estimate (SE) and coefficients of determination (r^2) for the equations indicated that the rates of ammonium adsorption in all soils could be best described by the pseudo second order, power function and simplified Elovich equations.

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РЕЗЮМЕ

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КИНЕТИЧЕСКАЯ АДСОРБЦИЯ АММИАКА НА НЕКОТОРЫХ ЛЁССОВЫХ ПОЧВАХ СЕВЕРНОГО ИРАНА

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Изучение кинетики адсорбции очень важно для понимания участвующих механизмов. Для того чтобы предсказать механизм, принимающий участие в настоящем процессе сорбции и потенциальную степень регулирующих этапов, таких как перемещение массы, процессов порозной диффузии и химической реакции, были использованы несколько кинетических моделей для соответствия экспериментальных данных, а именно, нулевого порядка, первого порядка, псевдо-второго порядка, упрощенный Elovich, параболические диффузии и модели функции силы. В данном исследовании, проводился кинетический эксперимент адсорбции аммония с использованием раствора, содержащего 100 мг/л хлорида аммония в течение 0,25 до 384 ч. Кинетические уравнения адсорбции аммония оценивали путем сравнения коэффициентов определения (r^2) и стандартных погрешностей оценки (SE) для каждого уравнения, которые определялись по методу анализа наименьшей квадратной регрессии. Результаты исследования кинетической адсорбции показали, что аммоний адсорбируется быстро в течение первых нескольких часов, но со временем, это происходит медленнее. Наиболее высокая адсорбция аммония наблюдалась в почве в Кордкоском районе, а низкая наблюдалась в почве в Хуттане 2. Степень адсорбции аммония во всех почвах можно лучше всего описать при помощи псевдо второго порядка, степенной функции и упрощенных уравнений Эловича.

Ключевые слова: адсорбция, аммоний, кинетический.

ТҮЙІН

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СОЛТҮСТІК ИРАННЫҢ КЕЙБІР САРҒЫШ ТОПЫРАҚТЫ ЖЕРЛЕРІНДЕ АММИАКТЫҢ КИНЕТИКАЛЫҚ СІҢІРІЛУІ

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Сіңіру кинетикасын зерттеу қатысушы тетіктерді түсіну үшін өте маңызды. Сіңіру үрдісіне қатысушы тетікті және массаның қозғалысы, жеке араласу үрдісі және химиялық реакцияны алдын ала болжау үшін эксперименталдық мәліметтерге сәйкес келу үшін бірнеше кинетикалық үлгі пайдаланылды, дәлірек айтқанда нөлдік реттегі, бірінші реттегі, жалған-екінші реттегі, жеңілдетілген Elovich, параболалық араласу және күш функциясының үлгісі.

Бұл зерттеуде 0,25 мен 384 с ішінде 100 мг/л аммоний хлоридін қамтитын ерітінді пайдаланумен аммонидің сіңіруіне кинетикалық тәжірибе жүргізілді. Аммонидің сіңіруінің кинетикалық теңгерілімі ең аз шаршылық кемімелді талдау әдісі бйынша анықталған әрбір теңгерім үшін бағалаудың стандартты кемшіліктері (SE) мен айқындау коэффициенттерін (r^2) салыстыру арқылы бағаланды.

Кинетикалық сіңіруді зерттеу нәтижелері көрсеткендей, аммоний алғашқы бірнеше сағат ішінде тез сіңіріледі, бірақ уақыт өте баяу сіңіріледі. Аммонидің ең көп сіңірілуі Кордкоск ауданында, ал ең аз сіңірілуі Хуттане 2 топырағында байқалды. Аммонидің барлық топыраққа сіңірілу деңгейін жалған екінші реттің, дәрежелік функция және Эловичтің жеңілдетілген теңгерімі көмегімен сипаттаған жақсы.

Кілтті сөздер: сіңіру, аммоний, кинетикалық.