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Characterization, isotherm and kinetic studies for ammonium ion adsorption by light expanded clay aggregate (*LECA*)

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Abstract The possibility of ammonium ion removal from aqueous solution using light expanded clay aggregate (*LECA*) was investigated in this work. FESEM and XRF analyses are used to determine the sorbent characterization. The influences of some effective parameters on ammonium ion adsorption process such as initial pH (3–9), initial ammonium ion concentration (10–100 mg/L), temperature (15–45 °C), and the contact time (0–180 min) were studied. Also, the equilibrium behavior of *LECA* in ammonium ion removal was investigated in the temperature range of 15–45 °C. The results showed that the equilibrium data were fitted well with two Langmuir and Freundlich isotherm models in all the studied temperature range. The maximum monolayer adsorption capacity estimated by Langmuir isotherm was obtained from 0.229 to 0.254 (mg/g). The required contact time to achieve the equilibrium condition was 150 min. Also, the regression coefficients of the kinetic models and more conformity of the experimental adsorption capacity (q_{exp}) to the calculated adsorption capacity (q_{cal}) were confirmed that the experimental data follow the pseudo-second-order kinetic model. The controlling rate of NH_4^+ adsorption process by the Webber–Morris model was proved both by film diffusion and intra-particle diffusion models.

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1. Introduction

Although nitrogen is an essential nutrient for all living organisms, it can be dangerous in high concentrations. The nitrogen compounds are one of the most important pollutants in water resource (Balci and Dince, 2002). Ammonium is an inorganic ion form of nitrogen impurity. High concentrations of ammonium lead to the growth of algae and plants resulting in reduction of dissolved oxygen in aqueous media and increment of

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botulism on aquatic organisms (Maranon et al., 2006). The pollution due to the ammonium effluents causes hazardous effects such as mortal, malady, water resources demolition, increased corrosion rate of soil materials, and in aquatic life causes coma, convulsion and even death (Balci and Dince, 2002; Randall and Tsui, 2002).

Various methods are used for ammonium ion removal from wastewater. The traditional method for ammonium removal is the biological treatment (nitrification–denitrification), however, it reveals a low performance in removal of high concentrations of ammonium (Zheng et al., 2008). In comparison to the biological processes, ion exchange or adsorption could be an effective and significant method (Singh and Prasad, 1997).

Some of the ammonium production sources as pollutant are coke plant, fertilizer factories, metal-finishing industries, farming activities, refrigeration systems, and sewage treatment plants (Singh and Prasad, 1997; Ghose, 2002; Li et al., 2003; Leakovic et al., 2000; Leinonen, 1999; Koivula et al., 2000). Also, many adsorbents were investigated in the literature for ammonium removal such as Zeolites (Zheng et al., 2008; Singh and Prasad, 1997; Ba and Ma, 2003; Lebedynets et al., 2004; Rozic et al., 2000), granular active carbon (GAC) Hussain et al., 2006; Aziz et al., 2004, and plant materials (Liu et al., 2006, 2010a,b; Saltali and Sari, 2006; Wahab et al., 2010).

More types of adsorbents for ammonium removal are used in laboratory scale applications due to the unavailability of materials in nature and being expensive. In recent years, the most efforts of researchers have been made to find the adsorbents with higher efficiency and lower cost (Sartape et al., 2010; González et al., 2011). Natural clays are one of the considerable and applicable sorbents due to their low-cost, availabilities and easy applications in removal of ammonia contaminants from environment (Balci and Dince, 2002). The various clays were used for ammonium ion removal such as *bentonite*, *sepiolite*, and *clinoptilolite* that were reported in the literatures (Balci and Dince, 2002; Maranon et al., 2006; Suzuki and Ha, 1984; Bernal and Lopez-Real, 1993).

Light expanded clay aggregate (*LECA*) is produced in a rotary kiln at the temperature of about 1200 °C. *LECA* consists of small, lightweight, bloated particles of burnt clay. It is a universally accessible and an environment-friendly, entirely natural product with a low cost and high porosity (Pioro and Pioro, 2004; Amiri et al., 2011). Review of the published articles indicated that *LECA* has been used as an adsorbent for removal of some toxic material and metals (Amiri et al., 2011; Haque et al., 2008; Dordio et al., 2010). For example, Haque et al. (2008) showed the performance of Iron-modified *LECA* for the removal of arsenic (V) from groundwater. Also, Dordio et al. (2010) studied the removal of pharmaceuticals in microcosm constructed wetlands using *LECA*.

The aim of this study was to assess *LECA* as a natural adsorbent to remove ammonium ion from the aqueous solution for the first time. Also, the adsorption mechanism of *LECA* and equilibrium behavior at different temperatures were investigated. The prepared adsorbents are characterized using appropriate techniques, including X-ray fluorescence (XRF) and field emission scanning electron microscopy (FESEM).

2. Materials and analytical method

2.1. Materials and characterization

LECA is a special type of clay pelletized and fired in a rotary kiln at a very high temperature (with grains size 4–10 mm). In this study, *LECA* was provided from Azarbayjani Company, Kermanshah, Iran. *LECA* was crashed and sieved through a 4–8 mesh size and then was washed to remove dust and undesirable components with deionized water for forth times and dried in an oven at 120 °C for 10 h until the weight became constant. Ammonium solution of 32% extra pure (Merck, Germany) was employed to prepare the stock solution containing 1000 ppm of ammonium ion which was further diluted with deionized water to the desired initial concentrations. The pH of the solution was adjusted using HNO₃ and NaOH by pH meter (827PH Lab Metrohm, Swiss made). All other materials were in analytical grade.

To characterize the physicochemical properties of *LECA*, field emission scanning electron microscopy (FESEM) and X-ray fluorescence spectroscopy (XRF) techniques were applied. The FESEM analysis was implemented using a Hitachi S-4160 (Japan), and the concentration of the major and trace elements in the resultant ash samples was determined using a wavelength XRF spectrometer (PW1480 Philips, and Netherland).

The concentrations of ammonia in the aqueous phase are determined using Nessler reagent. In this method, ammonia reacts with Nessler reagent forming a colored complex that varies from yellow to deep amber. The intensity of color is proportional to the ammonia content and is expressed as nitrogen in parts per million. The absorbance of ammonia (at 440 nm) is measured with a Perkin–Elmer UV/Vis spectrometer Lambda. Because the Nessler reagent has a pale color, the photometer should be zeroed with a reagent blank (BETZ Laboratories Inc, 1991).

2.2. Experimental set-up

The experiments were carried out in a fixed bed column of 9 cm inner diameter and height of 50 cm with ammonium solution as a liquid phase (wastewater) and *LECA* as adsorbent bed (fixed bed) that can be seen in Fig. 1. A metallic mesh was placed at the bottom of the bed as distributor, and up and down of the bed filled by non-combustible stone (inert bed). An electric heater and cooling water circulation system provided temperature control of solution (15–45 °C) and the flow was controlled by a flow meter adjusted in a constant value of 50 mL/min. The column was filled by 420 mg of *LECA*.

2.2.1. The experimental method

The ammonium adsorption capacity was calculated with the Eq. (1) Maranon et al., 2006:

$$q = \frac{(C_0 - C_f) \cdot V}{m} \quad (1)$$

where C_0 (mg/L) is the initial concentration of ammonium ion and C_f (mg/L) is the ammonium concentration in aqueous phase after adsorption. V is the total solution volume (mL) and m (mg) is the amount of sorbent on the dry basis.

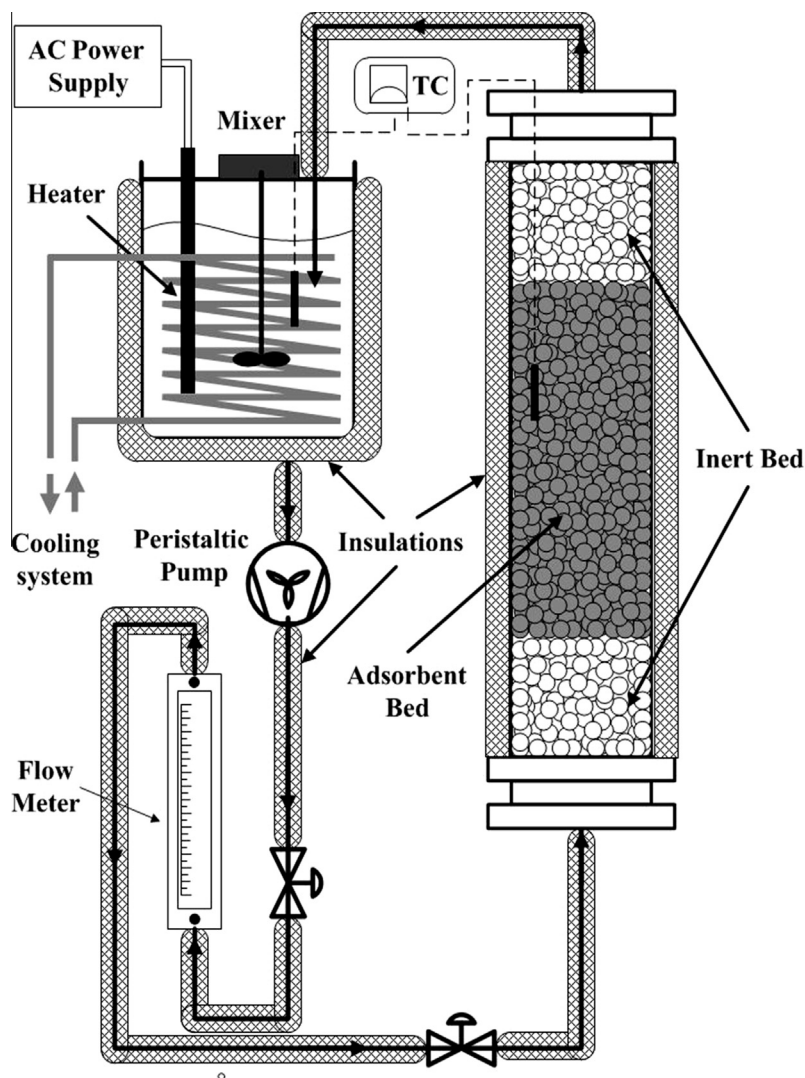


Figure 1 Schematic diagram of experimental set-up.

3. Results and discussion

3.1. Adsorbent characterization

Fig. 2 shows the FESEM images of *LECA*. The images captured from *LECA* surface confirm the high porosity of *LECA* particles as a good adsorbent. Moreover, *LECA* composition was characterized using XRF analysis and the data were reported in Table 1. Accordingly, the most part of *LECA* composition was SiO_2 (64.8%), Al_2O_3 (15.05%) and Fe_2O_3 (7.45%). Non-bonding electrons of oxygen in SiO_2 can constitute the complex with ammonium Ion in the solution. Therefore, it may be proved that the most important factor of Ammonium Ion Adsorption from aqueous solution is the abundant values of SiO_2 in *LECA* structure (Albuquerque et al., 2008).

3.2. Effect of contact time and initial ammonium ion concentration

The effect of the contact time on ammonium ion removal is shown in Fig. 3. The increment of contact time leads to the increasing of the ammonium ion uptake in the solution. As

it can be seen, the increase in ammonium adsorption capacity is rapid within the first 60 min. It can be due to the presence of unsaturated and active sites in the initiation of adsorption process and fast diffusion in the pores during the first 60 min (Karadag et al., 2006; Huang et al., 2010). By passage of time, pores are occupied due to ammonium ion adsorption causes to increase the ammonium ion adsorption capacity. But, with increasing of contact time, the driving force decreases (the concentration gradient) during mass transfer process that leads to increasing of ammonium uptake slowly until 120 min and reaches to the constant value after approximately 150 min considered as the equilibrium time (Hussain et al., 2006; Huang et al., 2010). This result is observed for all studied concentrations in this study which is shown in Fig. 3. Also, in the specified time, the ammonium uptake increases by increasing of the initial ammonium concentration (Balci and Dince, 2002).

3.3. The effect of pH

The pH is one of the main effective parameters in the ammonium adsorption process (Yusof et al., 2010). The effect of pH

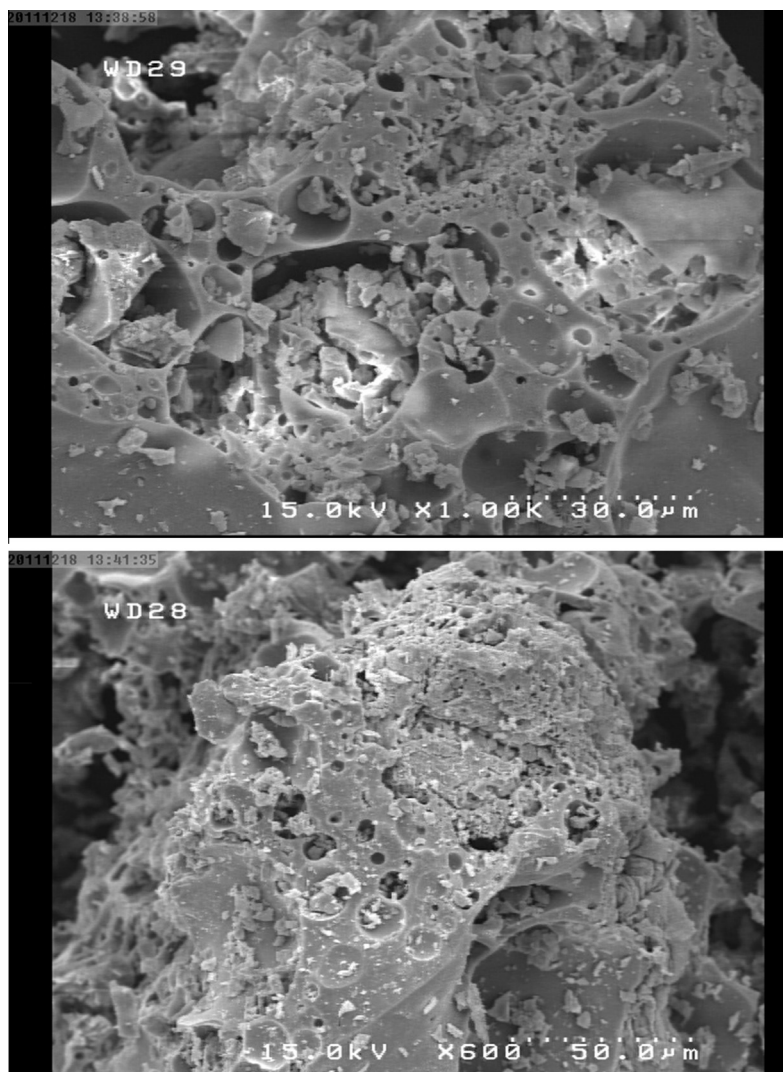


Figure 2 Field emission scanning electron microscopy (FESEM) of granular *LECA*.

Table 1 The characterization of *LECA*.

Constituent	Weight%
SiO ₂	64.83
Al ₂ O ₃	15.05
Fe ₂ O ₃	7.45
CaO	2.98
Na ₂ O	1.10
K ₂ O	2.55
MgO	3.67
TiO ₂	0.63
MnO	0.13
P ₂ O ₅	0.13
SO ₃	0.11
L.O.I.*	1.37

* Loss of ignition.

solutions. The equilibrium reaction of Bronsted–Lowry acid base reaction demonstrates that the cation-exchange process occurs only if in the following reaction (Eq. (2)), the ammonium removal is greater at lower pH values and smaller at higher pH values (Huang et al., 2010):



However, the ammonium adsorption capacity decreases at lower pH values, in low pH values, the competition between H⁺ and NH₄⁺, for occupation of the active sites on sorbent surface causes to decrease ammonium ion adsorption capacity. According to Eq. (2), at high pH values, the ammonium ion is transferred to NH₃ gaseous species. Then, it is predictable that the ammonium ion adsorption capacity declines at pH values higher than eight. The effects of various values of pH on ammonium adsorption capacity are presented in Fig. 4. The higher adsorption capacity amounts were obtained at pH range of 6–7 which is in agreement with the mentioned theory in Eq. (2). The optimum ranges of pH for ammonium adsorption were reported to be 5–8 and 5–7 by other researchers (Yusof et al., 2010; Liu et al., 2010; Ji et al., 2007).

on ammonium ion adsorption is investigated within pH range of 3–9 for the initial concentration of 80 mg/L of ammonium

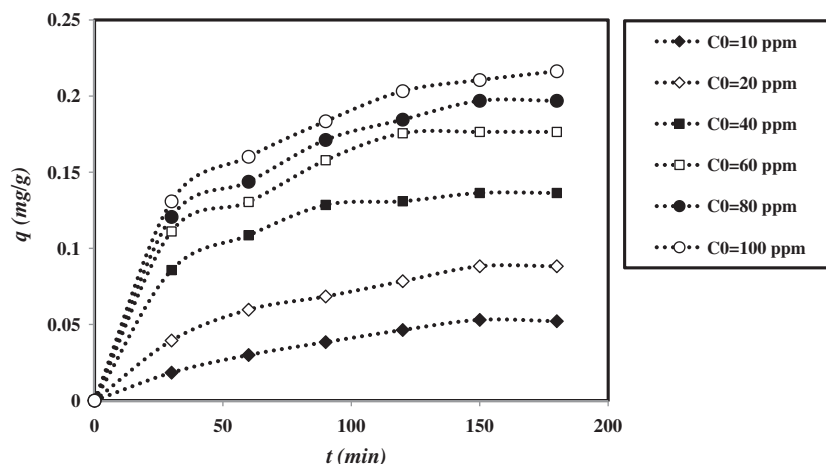


Figure 3 The effect of contact time on ammonium removal using LECA.

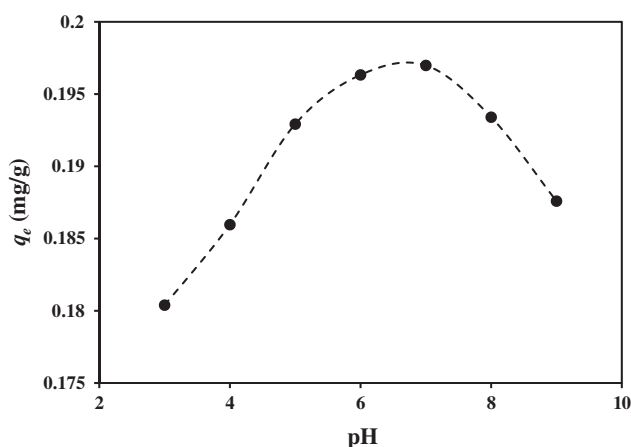


Figure 4 The effect of pH values on ammonium adsorption capacity.

3.4. The equilibrium studies

The study of equilibrium behavior of sorbent is necessary to design and optimize the adsorption systems (Yusof et al., 2010). The correlation between the adsorbent concentration in the liquid phase and the adsorption capacity at equilibrium time is presented by isotherm models. Among many isotherms investigating the adsorption mechanism, Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) are the most common isotherm models. In this study, the equilibrium behavior of the sorbent during ammonium ion adsorption was investigated by Langmuir and Freundlich models at different temperatures (15, 25, 35 and 45 °C). The Langmuir isotherm is based on monolayer coverage of adsorbent homogenous surface with the constant adsorption heat for all active sites that is given as Eq. (3):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

The linear form of Eq. (3) is Eq (4):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{4}$$

The dimensionless separation factor (R_L) is the essential characteristics of Langmuir isotherm which is expressed as Eq. (5):

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The value of dimensionless separation factor (R_L) defines the adsorption nature as:

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L value for all studied concentrations in this investigation is obtained below 1.0 and confirms that the ammonium adsorption is a favorable process.

The Freundlich isotherm is an empirical equation and is valid for heterogeneous surface. This model is expressed as Eq. (6):

$$q_e = K_F C_e^{1/n} \tag{6}$$

The linear form of Freundlich model defined by Eq. (7):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

where q_m (mg/g) and q_e (mg/g) are the maximum monolayer and equilibrium amount of NH_4^+ adsorbed per unit mass of sorbent respectively, C_e (mg/l) is the equilibrium ammonium ion concentration in the aqueous solution. C_0 (mg/l) is the initial amount of ammonium ion, K_L (l/mg) is Langmuir constant related to adsorption energy, K_F (mg/g) and $1/n$ (l/g) relate the adsorption capacity of the sorbent and the intensity of adsorption process (heterogeneity parameter), respectively. The value of the empirical parameter in the range of $1 < n < 10$ indicates a good and favorable adsorption (Ho and McKay, 1999). Fig. 5 shows the adsorption isotherm of ammonium ion with LECA at the initial concentration range of 10–100 (mg/L), for different temperatures 15, 25, 35 and 45 °C.

Langmuir and Freundlich isotherm models are depicted in Fig. 6. Also, the parameters of Langmuir and Freundlich isotherm model and their correlation coefficients are presented

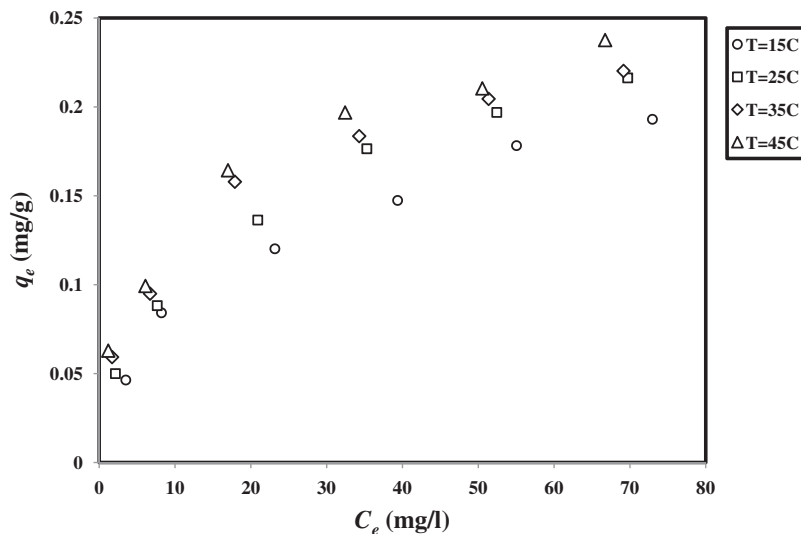


Figure 5 The experimental isotherm for ammonium ion onto *LECA*.

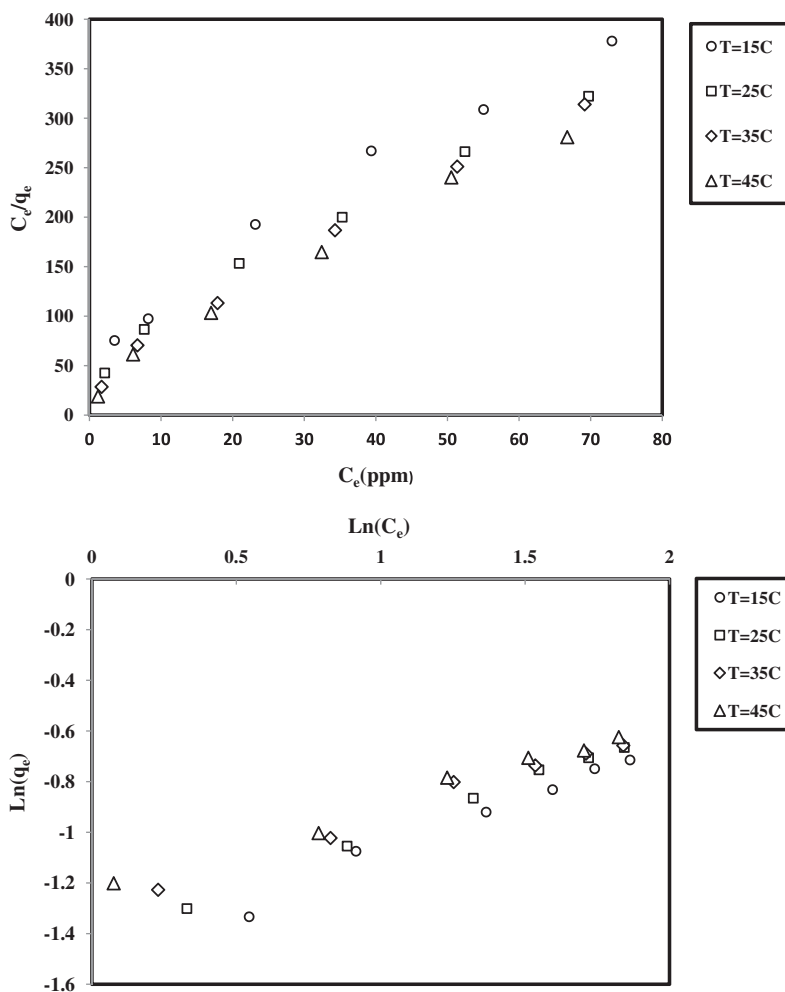


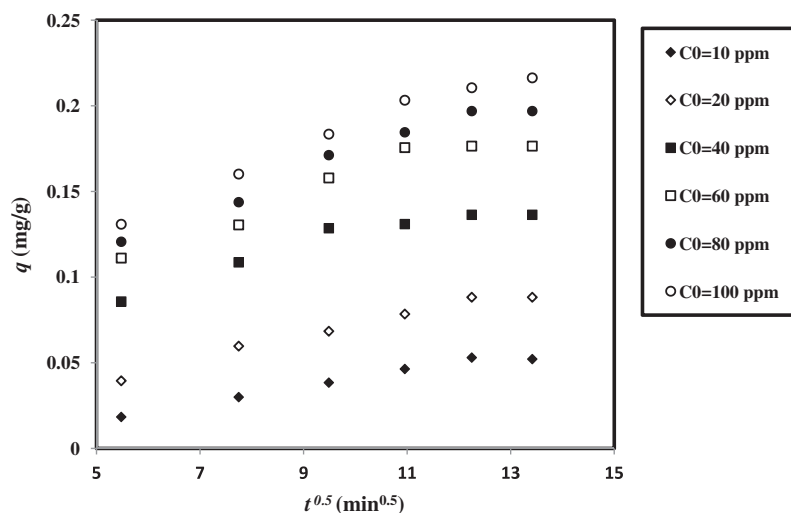
Figure 6 Langmuir (a) and Freundlich (b) isotherms for ammonium adsorption by *LECA*.

in Table 2. As it is observed from Fig. 6, two models can be fitted well with experimental data. This result was reported by (Maranon et al., 2006). The obtained results show that

the Freundlich isotherm has more correlation coefficient than the Langmuir isotherm. According to Table 2, the maximum monolayer adsorption capacity predicted by Langmuir

Table 2 Langmuir and Freundlich isotherm parameters for ammonium adsorption by *LECA*.

T(°C)	Langmuir parameters			Freundlich parameters		
	q_{\max} (mg/g)	K_L (l/mg)	R^2	K_F [(mg/g)(l/mg) ^{1/n}]	n	R^2
15	0.229	0.059	0.981	0.029	2.217	0.982
25	0.255	0.063	0.986	0.037	2.347	0.997
35	0.242	0.115	0.993	0.050	2.747	0.987
45	0.254	0.129	0.987	0.058	2.967	0.987

**Figure 7** The intra-particle diffusion model for NH_4^+ adsorption onto *LECA* at different initial concentrations.

isotherm was 0.255 (mg/g), at 25 °C. The amount of n parameter implies the desirable adsorption process and the high amount of coefficient K_F denotes the high intensity of ammonium ion for adsorption by *LECA* in all of the studied temperature. According to Table 2 increasing the temperature causes to increase the maximum monolayer adsorption capacity of *LECA* in ammonium ion removal. This is probably the result of the increasing of adsorbent pore size and maybe fluid viscosity decrease with temperature enhancement (Weng et al., 2007).

3.5. Adsorption kinetics

The different models were proposed to investigate the kinetic behavior of sorbents and examine the rate controlling stage. For this aim, the classic models namely, the pseudo first-order, pseudo second-order rate equation and intra-particle model were used in this paper. A model was proposed by (Weber and Morris, 1963) to study the intra-particle diffusion in adsorption processes explained as Eq. (8):

$$q_t = K_i t^{1/2} + C \quad (8)$$

where K_i (mg/min^{1/2}.g) is the intra-particle diffusion rate constant, q_t (mg/g) is the ammonium adsorbed amount per unit mass of *LECA*, t is the necessary contact time (min) and C is the intercept. The intra-particle diffusion model is depicted in Fig. 7 as the plot of q_t versus $t^{0.5}$. As it is shown from Fig. 7, the ammonium adsorption process is consisting of two stages: surface adsorption and intra-particle diffusion reported by Huang et al. (2010). The intra-particle diffusion rate

constant (K_i) for all initial concentrations are presented in Table 3. The driving force of the mass transfer increases with the increment of the ammonium initial concentration that can cause to decrease in the resistance against diffusion of the ammonium ions into the pores of *LECA*. It may be an acceptable reason for the increment of the intra-particle diffusion rate constant with the increasing of the initial concentration. The high regression coefficient values showed a good fitting between experimental data with this model.

According to the Webber and Morris model, the intra-particle diffusion can consider as the rate controlling stage if the plot of q_t versus $t^{0.5}$ passes from the origin (Weber and Morris, 1963). As can be seen from Fig. 7, the linear part does not pass through the origin. It can be implied the controlling stage of the ammonium ion adsorption onto *LECA* consists of the intra-particle diffusion and film diffusion (external diffusion) (Eq. (9) and Eq. (10)).

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 \cdot t}{2.303} \quad (9)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 \cdot q_e^2} \quad (10)$$

where K_1 is the rate constant of the pseudo-first-order adsorption process (min⁻¹), K_2 the pseudo-second-order rate constant of adsorption (g/mg.min). q_e and q_t are the amounts of ammonium ion sorbed (mg/g) at equilibrium and at time t (min), respectively Hussain et al., 2006; Freundlich, 1906. Figs. 8 and 9 show the plots of the kinetic models. The rate constant

Table 3 The kinetic parameters at various NH_4^+ concentrations.

C_0 (mg/L)	q_{exp} (mg/g)	Pseudo first-order			Pseudo second-order			Webber–Morris	
		q_{cal} (mg/g)	K_1 (min^{-1})	R^2	q_{cal} (mg/g)	K_2 (g/mg.min)	R^2	Ki (mg/g.min ^{1/2})	R^2
10	0.053	0.289	0.016	0.978	0.101	0.071	0.989	0.005	0.999
20	0.088	0.345	0.018	0.992	0.124	0.120	0.989	0.007	0.986
40	0.136	0.409	0.028	0.979	0.161	0.235	0.998	0.009	0.955
60	0.176	0.559	0.039	0.857	0.217	0.140	0.990	0.012	0.985
80	0.197	0.475	0.022	0.987	0.238	0.123	0.993	0.012	0.991
100	0.210	0.508	.0253	0.968	0.254	0.124	.996	0.012	0.989

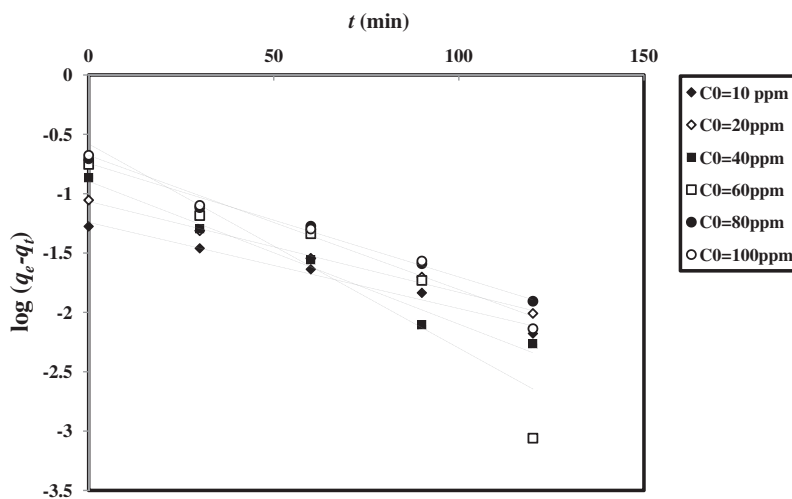


Figure 8 The pseudo-first-order reaction plot for NH_4^+ uptake onto *LECA* at different concentrations.

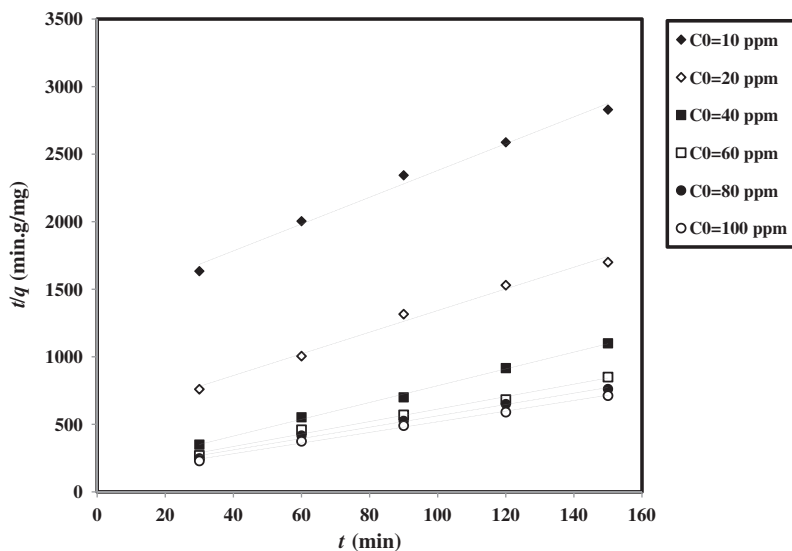


Figure 9 The pseudo-second-order reaction plot for NH_4^+ uptake onto *LECA* at different concentrations.

and the equilibrium ammonium uptake of the pseudo-first-order kinetic model were obtained from the slope and intercept of the plot $\log(q_e - q_t)$ versus t . Also, the rate constant and the equilibrium adsorption capacity were calculated from the intercept and the slope of the plot t/q_t versus t .

The parameters of kinetic models are listed in Table 3. The pseudo-first order model cannot describe kinetic behavior. R^2 values in this model are rather low and the calculated adsorption capacities (q_{cal}) are not in agreement with experimental values. The experimental data were fitted to the pseudo

second-order equation with higher R^2 values than pseudo-first order rate equation. The high correlation coefficients reveal the model success to describe the kinetics of ammonium adsorption. This result is in accordance with reported results by Liu et al. (2010); Hussain et al. (2006).

4. Conclusions

The application of *LECA* as adsorbent in NH_4^+ removal from aqueous solution was studied. The optimum pH was 7. Also, the equilibrium contact time for all ammonium ion concentrations was observed at 150 min. Langmuir and Freundlich isotherms were applied to test the equilibrium data. Both of Langmuir and Freundlich isotherms showed a good agreement with the equilibrium data in various temperatures. The maximum monolayer coverage capacity of *LECA* for ammonium adsorption was obtained as 0.255 mg/g, at 25 °C. The kinetic data followed the pseudo-second-order kinetic model. The rate-limiting step was consisting of both the film and intra-particle diffusion models. This paper presents *LECA* as a low-cost and green sorbent which can be used for ammonium ion removal. The variance analysis on the obtained data was also investigated. The calculated value was obtained around 0.003 that is close to zero. This verified that the data might be acceptable.

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