Journal of Saudi Chemical Society (2016) **20**, S342–S351

King Saud University

Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

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

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Received 6 June 2012; accepted 3 December 2012
Available online 20 December 2012

KEYWORDS

Ammonium removal;
LECA;
Equilibrium isotherm;
Adsorption kinetics

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.

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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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2012.12.003
1319-6103

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 Sarı, 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 HNO_3 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:

$$q = \frac{(C_\circ - C_f).V}{m} \tag{1}$$

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.