Desalination 277 (2011) 15–23

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Removal of ammonium from greywater using natural zeolite

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ARTICLE INFO

Article history:
Received 21 August 2010
Received in revised form 21 February 2011
Accepted 9 March 2011

Keywords:
Ammonium removal
Natural zeolite
Adsorption
Kinetics
Thermodynamics
Desorption

ABSTRACT

This paper focuses on the effectiveness of removing ammonium ion and the theoretical aspects of adsorption including adsorption isotherm, kinetics and thermodynamics as well as desorption–regeneration studies. Results have demonstrated that natural zeolite shows good performance with up to 97% for ammonium removal depending on contact time, zeolite loading, initial ammonium concentration and pH. The adsorption kinetics is best approximated by the pseudo-second-order model, whereas the adsorption isotherm results indicated that Freundlich model provides the best fit for the equilibrium data. Furthermore, with regard to thermodynamic parameters, it was found that Gibbs free energy change or adsorption energy ($\Delta G°$), −19.52 kJ/mol at 25 °C, −20.45 kJ/mol at 35 °C and −22.91 kJ/mol at 45 °C is negative indicating the spontaneous nature of the adsorption process, whereas the enthalpy change ($\Delta H°$), 30.96 kJ/mol is positive indicating endothermic adsorption process. The entropy change ($\Delta S°$), 0.169 kJ/(mol K) at 25 °C is also positive indicating increasing randomness at the solid-solution interface during adsorption. In addition, the desorption–regeneration studies demonstrated that desorption of ammonium on the zeolite is sufficiently high using NaCl solutions.

1. Introduction

Greywater is wastewater originated from bathroom and laundry in households. Ammonium is one of the significant greywater contaminants that is found in bathrooms because of urine [12], in kitchen from the use of ammonium salts as acidity regulators, thickeners and stabilisers [24] and in laundry wastewater due to the use of cationic surfactants such as quartenary ammonium salts, dialkyldimethylammonium chlorides, distearyldimethylammonium chloride and alkyldimethylbenzylammonium chlorides in fabric softeners and laundry disinfectant agents [2,15,18].

Although ammonium is a very important nutrient for algae, the excessive presence of ammonium in water streams and effluent causes eutrophication of estuaries, rivers, lakes and coastal seas [25] as well as corrosion/biological fouling problems in industrial water system [11] due to the growth of algae blooms. On the other hand, with the increasing issue of water reuse, ammonium is one of grey water contaminants that need to be removed due to health concerns especially for bathroom wastewater and swimming pool wastewater reuse.

Existing methods of ammonium removal are biological nitrification–denitrification, air-stripping and ion-exchange [7]. Among the various methods, ion-exchange is more competitive over air-stripping and biological methods due to little influence at low temperature. Moreover, ion-exchange takes up relatively little space particularly its relative simplicity of application and operation [7] as well as environmentally friendly [10]. Ion-exchange, therefore, seems to be an attractive method especially when low cost materials are used [27].

Natural zeolites are an abundant cation exchange material that is economically feasible for water and wastewater treatment. They have high selectivity toward water contaminants such as heavy metals reached up to 1800 mg/g [28] and ammonium ion reached up to 90% [26]. In addition, natural zeolites have advantages over other cation exchange materials such as organic resins [26] because they provide low-cost treatment, exhibit excellent selectivity at low temperatures, release non-toxic exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) to the environment [19], compact size in relatively little space and simply operation as well as easy maintenance of the full-scale applications [6,7]. Natural zeolites, therefore, gained significant interest over the last two decades especially with regard to eliminating or at least reducing water pollution problems.

Natural zeolites are composed of three dimensional frameworks of aluminosilicate tetrahedral where the aluminum and silicon structure atoms are bound by covalent bonds over common oxygen atoms to form interconnected cages and channels [10]. Each aluminum (Al^{3+}) atom substitution for silicon (Si^{4+}) in the zeolite framework generates one negative charge on the framework. The greater the aluminum atom substitution, the higher the negative charge of zeolite [23]. The negative charge within the pores is balanced by positively

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doi:10.1016/j.desal.2011.03.030

charged ions (cations) such as Na^+, K^+, Ca^{2+}, Mg^{2+} on the external surface of zeolite [25]. These cations are bound with aluminosilicate structure by weaker electrostatic bonds that cause ability of being exchanged with certain cations in solutions [13]. With the unique structure, natural zeolites possess high cation-exchange capacity, adsorption and molecular sieve capabilities.

Considerable research has been conducted to investigate various aspects of ammonium removal from waters and wastewaters by natural zeolites [10,25,37]. Structural characteristic of the zeolite used (e.g., mordenite, clinoptilolite, erionite, chabazite and phillipsite) affects cation exchange capacity of natural zeolites to remove ammonium from aqueous solution [23]. Furthermore, cation exchange capacity depends upon the nature of the cation (size, load, etc.), contact time, zeolite loading, initial anion concentration, pH and temperature. [4,5,23,26]. Obviously, capacity and performance of zeolite for ammonium removal cannot be predicted by a single zeolite chemical–physical parameter. A lab scale study, hence, is a need to evaluate the influence of variables on Australian natural zeolite performance when ion-exchange is used for the practical application of ammonium removal. From the survey of the literature, few research of ammonium removal has been conducted using Australian natural zeolite. Furthermore, no research has been focussed on adsorption isotherm, kinetics and thermodynamics using Australian natural zeolite to remove ammonium with consider greywater characteristics.

The main purpose of this research, therefore, was to consider a kind of Australian natural zeolite including defining the influence of various parameters on capacity and performance of the zeolite to remove ammonium efficiently from aqueous solution. In addition, desorption of the ammonium exchanged on the zeolite was also investigated. Theoretical aspects of adsorption such as adsorption isotherm, kinetics and thermodynamics of adsorption were also evaluated. Various models of adsorption isotherm and kinetics were determined based on statistical error analysis to find out the best-fit equation.

2. Methodology

2.1. Zeolite characterisation

In order to confirm the crystal structure and the mineralogy of the zeolite, X-ray Diffraction (XRD) analysis was performed using CuKα radiation. Chemical composition of the zeolite samples was determined by using X-ray Fluorescence (XRF) and Scanning electron microscopy-Energy dispersive spectroscopy (SEM-EDS). Surface morphology of the zeolite was determined using scanning electron microscopy (SEM).

The total cation exchange capacity (CEC) [11] and the external CEC (ECEC) were measured with a method modified from Ming and Dixon [22].

2.2. Batch study for ammonium removal using natural zeolite

For studying the effect of contact time on kinetics, the rate of ammonium removal by natural zeolite from aqueous solution was carried out to determine the optimum time required to reach equilibrium. Equilibrium test was determined by shaking of 5 mg/L and 50 mg/L ammonium chloride with zeolite/liquid ratio of 1 g/100 mL for varying times from 15 to 250 min at 25 °C. For determining zeolite loading effect, zeolite loading was varied from 0.5 to 3 g/100 mL. The zeolite-liquid was then shaken for 8 h at temperature 25 °C and ammonium concentration 5 mg/L. Moreover, to study the effect of initial ammonium concentration and adsorption isotherm, batch sorption was conducted by varying the initial ammonium concentration of 5–120 mg/L with zeolite/liquid ratio of 1 g/100 mL for 8 h at temperature 25 °C. Effect of pH was also studied by varying the initial pH solution from 2 to 10. At zeolite/liquid ratio of 1 g/100 mL and ammonium concentration of 50 mg/L, batch sorption was conducted for 8 h at temperature 25 °C.

For thermodynamics study, temperature of sorption isotherms was studied at 25, 35 and 45 °C. A 100 mL of ammonium chloride solution at concentration of 50 mg/L was equilibrated with 1 g zeolite for 8 h. Furthermore, adsorption–desorption experiment was conducted at ammonium concentration 80 mg/L and solid/liquid ratio 1 g/100 mL for three cycles. First, ammonium sorption was conducted until equilibrium was reached. Once equilibrium was reached, the saturated zeolite was separated from solution and added to 1% NaCl solutions until it reach a new equilibrium, when the ammonium concentration of two consecutive samples remained constant.

To study reversibility of ion exchange isotherm of ammonium on zeolite, adsorption experiment was conducted at solid/liquid ratio of 1 g/100 mL and temperature 25 °C by varying ammonium concentration from 1 to 80 mg/L. Once equilibrium was reached, desorption experiment was conducted by adding 1% NaCl solutions until a new equilibrium was reached. For all of batch experiments studied above, the suspension of each test was centrifuged and filtered through a 0.45 μm membrane filter. The initial and final concentrations were analysed according to the standard method [1]. Ammonium concentration was then analysed by employing a spectrophotometer based on standard phenate method.

The amount of contaminant absorbed from the aqueous solution was expressed as ammonium removal capacity per unit mass of the zeolite (q) as:

$$q = \frac{(C_o - C_e)V}{m} \tag{1}$$

where, C_o is the initial ammonium concentration (mg/L), C_e is the equilibrium ammonium concentration (mg/L), V is the batch volume (L) and m is the zeolite mass (g).

The percentage of ammonium removal efficiency from the aqueous solution was then calculated from:

$$\text{Removal efficiency } (\%) = \frac{(C_o - C_e)}{C_o} \times 100\% \tag{2}$$

2.3. Kinetic data analysis

Four kinetic models were used in order to investigate the adsorption process of contaminants onto the adsorbents and they are pseudo-first-order, pseudo-second-order, Bangham, intra-particle diffusion models and Elovich. The data were processed and fitted to kinetic equations.

First, the pseudo-first-order is the equation used commonly to describe adsorption and it is determined by the following Eq. (3).

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{3}$$

where q_t (mg/g) is the amount of adsorbate adsorbed at time t (min), q_e (mg/g) is the equilibrium adsorption capacity mg/g), and k_f (min^{-1}) is the rate constant of pseudo-first-order model (min^{-1}). The equation can be integrated by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes

$$ln(q_e - q_t) = \ ln q_e - k_1 t \tag{4}$$

The pseudo-second-order model can be expressed in the form

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{5}$$