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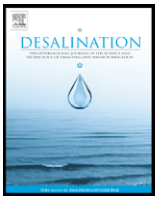

Principles of interaction of ammonium ion with natural Jordanian deposits: Analysis of uptake studies

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ABSTRACT

Ammonium ion removal from aqueous solution by Petra clay minerals has been established. To study the efficiency of the Petra clay as sorbent, the effect of relevant parameters, such as temperature, contact time, pH and initial ammonium (NH_4^+) concentration were examined. Kinetics experiments were also done at different parameters. The pseudo first-order, pseudo second-order kinetic models and intra-particle diffusion model were used to describe the kinetic data. The pseudo second-order kinetic model provided excellent data fitting ($R^2 > 0.99$), and the rate constant for sorption was predicted. Activation energy of sorption has also evaluated as 22.60 kJ/mol based on the pseudo second-order rate constants, the findings of this investigation suggest that physical sorption plays a role in controlling the sorption rate. Ammonium uptake rate was controlled by particle diffusion at different variables.

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1. Introduction

Many natural and industrial feed waters requiring treatment contain a mixture of polluting ions, many of which may be removed by ion exchange [1–4]. However, one of the common toxic pollutants is ammoniacal nitrogen (NH_3 and NH_4^+). This may be initially present in, for example, municipal or food industry wastewater, but may also be produced as a result of biological modification of organic nitrogen during other treatment operations. The industrial contexts of this problem include oil refineries, coal gasification plants, slaughter-houses, dairy plants, distilleries, fertilizer plants and pharmaceutical operations.

The discharge of effluent waters containing ammonia and ammonium ion is coming under increasingly strict concentration limits for discharge [5,6].

Ammoniacal nitrogen is present in two forms when in water: ammonia (NH_3 or NH_4^+), according to Eqs. (I) and (II)

$$NH_4^+ + H_2O \leftrightharpoons NH_3 + H_3O^+ \tag{I}$$

$$NH_4^+ + H_3O^+ \leftrightharpoons NH_3 + H_2O \tag{II}$$

The traditional method for ammonium removal from municipal and industrial wastewater is based on biological treatments. Since biological methods (nitrification–denitrification) do not respond well to shock loads of ammonia, unacceptable peaks may appear in the effluent ammonium concentration. As discharge limits of various pollutants become more stringent, ion exchange and adsorption become more interesting as possible treatment methods. Ion exchange with natural silicate minerals is more competitive because of its low cost and relative simplicity of application and operation. The use of natural silicate for removal of ammonium ion from water and wastewater appears to have potential due to the advantages and peculiarities over some conventional and expensive ion exchange resins [7].

In the aqueous solution, ammonium can exist in either the non-ionized form and/or ionized form depending on the pH and temperature. Of the two forms of ammonium, only the ionized one can be removed by the ion exchange process [8,9].

The present work considers ammonium removal by a natural ion exchange resin which is Petra clay.

This investigation concentrates on defining various operational parameters necessary to remove ammonium efficiently through ion exchange by using Petra clay from aqueous solutions. The adsorption kinetics was also considered.

However, little investigation has been conducted to determine the kinetics of ammonium exchange using natural silicates. The diffusion mechanism of the process of the zeolite in ammonium uptake was in the focus of this study.

1.1. Kinetics of ammonium exchange

1.1.1. Pseudo first-order model

The pseudo first-order model (Lagergren) equation kinetics can be written as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{1}$$

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where q_e is the equilibrium amount of NH_4^+ exchanged by the silicates (mg/g), q_t is the amount of NH_4^+ exchanged at any time t, and k_1 is the rate constant (min^{-1}).

1.1.2. Pseudo second-order model

The pseudo second-order rate model is represented as

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

where k_2 is the rate constant of pseudo second-order sorption ($\text{g mg}^{-1}\text{min}^{-1}$). Values of k_2 and q_e were obtained from the straight-line plots of t/q_t against t [10–12].

1.2. Ion exchange modeling

In order to determine the rate-controlling step of the process to evaluate the diffusion coefficient, the particle and the diffusion models were used. Vermeulen's model for the fractional attainment equilibrium, $U(t)$, given particle diffusion control with infinite volume boundary conditions, is written as

$$U(t) = \left[-1 \exp\left(\frac{-D_p \pi^2 t}{r_p^2} \right)^{1/2} \right] \tag{3}$$

where $U(t)$ is defined as the ratio between ammonium mass sorbed at a certain time and the maximum ammonium sorbed, D_p is the diffusion coefficient in the ion exchanger expressed in m^2/s and r_p is the radius of the particle (m).

The film diffusion control model with infinite boundary conditions is described by the following equation:

$$U(t) = 1 - \exp\left(\frac{-3 D_f C t}{r_p \delta C^*} \right) \tag{4}$$

where D_f is the diffusion coeffcient in the film (m^2/s), C and C^* are the ammonium concentrations in the solution and in the ion exchanger, respectively (mol/L), δ is the film thickness accepted as 10^{-4}cm for poorly stirred solution.

Eqs. (3) and (4) can be rearranged to give Eqs. (5) and (6).

$$-\ln(1 - U(t)^2) = t\left(\frac{D_p \pi^2}{r_p^2} \right) \tag{5}$$

$$-\ln(1 - U(t)) = t\left(3 \frac{D_f C}{r_p \delta C^*} \right) \tag{6}$$

To find D_p and D_f, $-\ln(1-U(t)^2)$ and $-\ln(1-U(t))$ will be plotted against the time t [13].

The percent ammonium uptake (q_e) was calculated using the following equation:

$$\%q_e = \frac{(C_o - C_e)V}{M} \times 100 \tag{7}$$

where q_e (mg/g) is the amount of the total adsorbed ammonium ions, C_o and C_e are the initial and equilibrium concentrations of ammonium in solution (mg/L), respectively. V (L) is the solution volume and M (g) is the adsorbent weight.

2. Experimental

2.1. Material and methods

2.1.1. Clay treatment

Raw clay sample was obtained from Jordanian local location; the sample was washed to remove the water soluble residues and other undesirable materials. In order to avoid comminution, washing was achieved by soaking the clay in deionised water for 24 h with regular gentle agitation. The material was then soaked successively in a series of batches of 10% sodium nitrate solution for periods of approximately 12 h over a period of 7 days in order to ensure complete conditioning into sodium form. The clay was then washed to remove excess $NaNO_3$ and dried at 97 °C until constant weight at room temperature, and stored in polyethylene flasks for further experiments. The sample was crushed and classified to a size range 38–250 µm using ASTM sieve.

The mineralogical composition of this clay was investigated by means of the X-ray diffraction (XRD) for raw clay, the scanning electron micrograph (SEM), and the chemical composition for the treated clay was investigated by using X-ray fluorescence (XRF) as shown in Table 1 can be seen in the previous works [14,15], the physical properties are also investigated and shown in Table 2.

2.1.2. Test chemicals and analysis

Ammonium nitrate stock solution (1000 mg/L NH_4^+) was prepared by dissolving NH_4Cl in deionised water. The solution was further diluted before use. Ammonium chloride and other chemicals used were of analytical grade. Synthetic samples were prepared to give different ammonium concentrations. The ammonium concentration of the samples was determined by the standard Nesslerisation method using UV/Vis Spectrometer (UNICAM 900). It should be noted that no more than 5 mL of sample was taken for measurement of ammonium, and the total volume of the aqueous solution was affected insignificantly.

2.1.3. Batch experiments

The ion exchange of NH_4^+ ion on clay was carried out using a batch method. The batch experiments were conducted using 1.0000 g of adsorbent with 25.0 mL ammonium solution in the range of 5–100 mg/L initial concentration.

The effect of the contact time was also studied by conducting also 1.0000 g of adsorbent with 25.0 mL of 10 mg/mL ammonium solution, the time of analysis was, 5, 10, 15 min, then the interval of analysis was expanded to 0.5 h, 1 h, 2 h, 4 h, 6 h, 8 h and 24 h. The percent removal of every taken sample was calculated.

The influence of the pH of the range (4–10) on the removal of the ammonium ion was investigated using exactly 1 g of the adsorbent with 10 mg/mL ammonium solution, the percent removal was calculated for every single pH in order to obtain the suitable pH for this study.

Table 1
Chemical composition (wt.%) of treated clay sample (obtained by XRF analysis).

Compound	Percent
SiO_2	44.97
Fe_2O_3	9.32
Al_2O_3	20.85
MgO	1.123
CaO	17.81
TiO	1.20
K_2O	3.33
Na_2O	0.07
MnO	0.04
P_2O_5	0.07

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