

# Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite

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## Abstract

Ammonium removal from aqueous solution by a natural ion-exchange resin was investigated by considering the factors affecting the ammonium-exchange capacity including the zeolites' particle size, the loading flow rates and the impact of a number of regenerations upon the ion-exchange capacity. The resin column was exhausted by downflow at 10, 25, 50 and 75 bed volume (BV)/h, until effluent ammonium concentration of more than 10 mg/l  $\text{NH}_4^+$  was achieved. The results indicate that conditioning of the zeolite improves the ion-exchange capacity and that the smaller particle size also causes a higher ion-exchange capacity due to greater available surface area. The actual ion-exchange capacity of the conditioned fine (-1.00+0.125) and coarse (-2.00+1.00) mm clinoptilolite was found to be 0.57 and 0.38 meq/g zeolite, respectively.

## Introduction

Zeolites are aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations (normally  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ ) in addition to water in their structural framework. The physical structure is porous, containing interconnected cavities in which the metal ions and water molecules are contained. Clinoptilolite is one of the natural zeolites used to remove cations such as heavy metals (Ahmed et al., 1998; Ouki and Kavannagh, 1999; Callejas et al., 2001) and ammonium ions from aqueous solutions (Mercer et al., 1970; Koon and Kaufman, 1975; Jorgensen and Barkacs, 1976; Klieve and Semmens, 1980; Schoeman, 1986).

The zeolite-rich tuffs of Bigadiç, in the northwestern part of Turkey, are mainly coarse-grained, glassy, with ash tuffs on top (Sirkeciolu and Senatlar, 1995). The availability of natural zeolites in many countries facilitates low-cost treatment by ion-exchange systems (Mercer et al., 1970). The use of clinoptilolite as a resin has the following advantages:

- good performance of ammonium removal under low temperature;
- compact size and easy maintenance of the full-scale plants; and
- ammonium-ion selectivity (Singh and Prasad, 1997).

The widespread application of ion-exchange processes has led to the development of equipment that functions almost automatically and requires relatively little maintenance. While the total exchange capacity of clinoptilolite is somewhat less than that of synthetic organic resins, its selectivity for the ammonium ion gives it a distinct advantage over conventional exchange resins.

Among the technologies for ammonium control are such processes as air stripping, breakpoint chlorination, nitrification-denitrification and ion-exchange (Metcalf and Eddy, 1991). Ion-exchange seems to be an attractive method especially when low-cost minerals can be used as an exchanger.

Ammonium removal from aqueous solution by ion-exchange has been investigated by many researchers (Koon and Kaufman, 1975; Gaspard et al., 1983; Schoeman, 1986; Haralambous et al., 1992). Koon and Kaufman (1975) were concerned with ammonium removal from municipal wastewater by clinoptilolite. Gaspard et al. (1983) examined the ammonium removal characteristics from drinking water by clinoptilolite. Schoeman (1986) evaluated  $\text{NH}_3\text{-N}$  removal from an underground mine-water by South African clinoptilolite (Pratley) and compared it with Hector clinoptilolite from the USA. Haralambous et al. (1992) compared natural and synthetic zeolites for ammonium removal from aqueous solution.

In the aqueous solution, ammonium can exist in either the non-ionised form ( $\text{NH}_3$ ) and/or ionised form ( $\text{NH}_4^+$ ) depending on the pH and temperature. Of these two forms of ammonium, only the ionised one can be removed by the ion-exchange process. The equilibrium-exchange capacity remains constant up to pH 7. For optimum ion-exchange operation, the pH of the aqueous solution must be at or below 7.

Ion-exchange is an endothermic process. Hence, an increase in temperature tends to increase the exchange capacity of this process (Lin and Wu, 1996).

During the ion-exchange process, the  $\text{Na}^+$  ion is replaced by the  $\text{NH}_4^+$  ion, and hence the  $\text{Na}^+$  ion concentration increases in the liquid phase during the ion-exchange processes. When the ion-exchanger reaches breakthrough, the upflow or downflow regeneration method is applied. Gaspard et al. (1983) reported that the upflow regeneration is more attractive than down-flow regeneration.

The ammonium ion-exchange capacity varies depending on the presence of another cations in the aqueous phase and initial ammonium concentration (Gaspard et al., 1983; Lin and Wu, 1996; Singh and Prasad, 1997; Demir et al., 1998). The ion-exchange capacity is influenced significantly by chemical and physical pretreatment techniques and loading or regeneration of clinoptilolite. The influence of a pretreatment on ion-exchange capacity varied widely depending on the source of clinoptilolite (Klieve and Semmens, 1980).

The present work considers ammonium removal by a natural ion-exchange resin. This investigation concentrates on defining various operational parameters necessary to remove ammonium efficiently through ion-exchange by using the zeolite, clinoptilolite. The main objective of this study is to evaluate the capacity of

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