

## Ammonia removal capacity of European natural zeolite tuffs: application to aquaculture waste water

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**Abstract.** The possibility of improving aquaculture water quality using different kinds of zeolites is discussed. Zeolites are aluminosilicates, whose framework structure allows them to exchange cations. Cations have differing affinities for different structures, and in particular ammonia has a great affinity for phillipsite and clinoptilolite structures. These zeolites are already used for ammonia removal from municipal piggery, and aquacultural wastes. In the present paper, ammonia removal from aquacultural water from recirculating systems has been tested, comparing different zeolites under laboratory conditions. Phillipsite and clinoptilolite tuffs were effective in ammonia removal, while chabazite tuff having a lower content of zeolitic material (50%) and lower affinity for ammonia showed that a lower temperature did not influence ion exchange capacity in any of the zeolites.

### Introduction

A zeolite is a framework of aluminosilicate whose structure contains channels filled with water and exchangeable cations. The negative charge of the framework is balanced by alkalis and alkaline earths located in the channels. This structure allows zeolites to exchange cations with a capacity ranging from 2.16 meq/g to 4.73 meq/g (Mumpton 1984). Because of their structure, zeolites are ion selective. In general, the preferred ions have a small charge and large size (Passaglia 1991). The most commonly represented framework-linked ions are  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Fe^{2+}$ , more rarely  $Li^+$ ,  $Sr^{2+}$  and  $Ba^{2+}$  (Vaughan 1978).

The affinity of zeolites for  $NH_4^+$  is the basis of much of their use in animal husbandry and aquaculture (Mumpton & Fishman 1977). In intensive aquaculture, efficient removal of  $NH_4^+$  is of the utmost importance (Piper 1984).

In Italy, six zeolitic tuffs are found (phillipsite, chabazite, clinoptilolite, mordenite, laumontite and analcime), but only phillipsite and chabazite are utilized, as they are available in deposits forming up to 70% of the total volume of rock (Passaglia & Galli 1991).

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Clinoptilolite is one of the most studied zeolites (Horsch & Holway 1984; Mumpton 1984; Piper & Smith 1984); however, Italian zeolite tuffs (phillipsite and chabazite) have been tested in a number of trials (Hagiwara & Uchida 1978; Murphy, Hrycyk & Gleason 1978; Colella, Aiello & Nastro 1984; Dryden & Weatherley 1987; Bergero, Di Natale, Forneris & Palmegiano 1991a,b; Bergero, Boccignone, Di Natale, Forneris & Palmegiano 1992). The present paper examines the comparative  $\text{NH}_4^+$  ion exchange efficiency of phillipsite, chabazite and clinoptilolite under controlled conditions, and demonstrates the performance of phillipsite in an experimental trout-rearing system.

## Materials and methods

### *Ammonia adsorption trials*

In a first set of trials the  $\text{NH}_4^+$  removal capacity was studied by means of a  $2 \times 3$  design with two replicates, with starting  $\text{NH}_4^+$  concentrations of 2.5 mg/l and 10 mg/l. This study was run in six pairs of aquaria with recirculated deionized water, each circulated by a centrifugal pump at a flow rate of up to 2 l/min. Each pair of tanks contained 45 l deionized water. A daily make-up was provided to compensate for evaporation. Samples of circulating solutions were taken at 0, 3, 6, 12, 24 and 48 h. Test zeolites – 100 g of chabazite tuff containing about 50% chabazite, or phillipsite tuff containing 60% phillipsite – were interposed as a filtering layer between the two tanks of each pair. The cation exchange capacities of the two zeolites were respectively 3.84 meq/g and 3.31 meq/g (Mumpton 1984). The removal capacity was studied on new materials and after regeneration which was carried out using three volumes of NaCl 1 M, and subsequently washed by one volume of distilled water, at a flow rate of 10 ml/min. All ammonia adsorption tests were performed at a flow rate of 100 l/h.

Subsequently, phillipsite tuff and a clinoptilolite tuff from Zlatokop (Macedonia) containing about 90% zeolite (Artioli, Alberti, Cagossi & Bellotto 1991) were tested in the same conditions; clinoptilolite has an exchange capacity of about 2.16 meq/g (Mumpton 1984). The same system of tanks was used with  $\text{NH}_4\text{Cl}$ , at an initial concentration of 10 mg/l with four replicates.

Sample of 100 g were used before and after regeneration using 3, 10 and 24 bed volumes of NaCl 1 M.

Ammonia determination was carried out by an Ion-Analyzer EA 940 equipped with an Orion Research specific ion electrode system for  $\text{NH}_4^+$ .

### *Ammonia enrichment tests*

The response of the zeolites to rising ammonia concentration was studied using a daily intake of 2.5 mg/l ammonia added to an initial concentration of 10 mg/l, simulating the presence of a medium stocking density of rainbow trout, *Oncorhynchus mykiss* (Walbaum) (Dabrowski 1986; Gongnet, Mayer-Burgdorff, Beker & Guenther 1987). Samples of solutions were collected daily for ammonia determination.



### Fish-rearing tests

The efficiency of phillipsite in trout rearing was studied by monitoring ammonia removal over 3 weeks in 250-l tanks with a complete water-recirculating system at a flow rate of 60 l/min (operated by EHEIM filter pumps filled with glass wool and 500 g of, respectively, phillipsite or/and activated charcoal) and a stocking density of 4 kg/m<sup>3</sup> of 100 g trout.

Trout were kept fasting or fed 1.2% wet weight of a commercial diet containing 47% crude protein, using no filtering materials, to determine ammonia excretion in the same tanks at 12°C, over 7 days. In the final stage, two stocking densities (4 and 6 kg/m<sup>3</sup>) of 100 g trout were reared in the same conditions, using phillipsite as filtering material. Ammonia level was monitored every 48 h, from the 21st day onwards.

### Data analysis

In adsorption experiments, NH<sub>4</sub><sup>+</sup> concentrations were plotted against time and the final values tested by ANOVA (analysis of variance) (Snedecor & Cochran 1982). All statistical analyses were carried out using Statgraphics software (Statistical Graphics Corporation, Inc. 1988).

In the ammonia enrichment and trout-rearing trials, trends of ammonia concentrations were plotted against time; slopes of linear regressions were compared by means of Student's *t*-test (Scossiroli & Palenzona 1971).

### Results and discussion

The final NH<sub>4</sub><sup>+</sup> concentrations in the preliminary experiments are shown in Table 1. The initial concentrations chosen (2.5 and 10 mg/l) are typical of intensive and hyperintensive stocking densities respectively (Dabrowski 1986; Gongnet *et al.* 1987). Regeneration improved NH<sub>4</sub><sup>+</sup> removal capacity of both zeolitic tuffs; similar results had already been obtained by Collella *et al.* (1984).

The zeolitic tuffs were found to remove NH<sub>4</sub><sup>+</sup> effectively at both 2.5 mg/l and 10 mg/l concentrations. Statistical analysis showed significant differences in removal capacity between phillipsite and chabazite: phillipsite gave better results at both concentrations. This accords with the higher percentage of zeolitic material and higher affinity for NH<sub>4</sub><sup>+</sup>,

**Table 1.** Final NH<sub>4</sub><sup>+</sup> concentrations (ppm) in the preliminary adsorption experiments (means  $\pm$  SD)

	Initial concentration	
	2.5 ppm	10 ppm
Virgin chabazite	1.04 $\pm$ 0.11	3.30 $\pm$ 0.57
Virgin phillipsite	0.66 $\pm$ 0.16	2.06 $\pm$ 0.06
Regenerated chabazite	0.35 $\pm$ 0.04	1.79 $\pm$ 0.40
Regenerated phillipsite	0.16	0.72 $\pm$ 0.10

as reported by Sherman (1978). In the preliminary trials, ANOVA showed significant differences ( $P < 0.001$ ) between the final ammonia concentrations: phillipsite (0.39 mg/l), chabazite (0.69 mg/l), at lower concentrations.

Similar results were also obtained at high concentrations: phillipsite (1.28 mg/l); chabazite (2.51 mg/l), with  $P < 0.001$ . Regeneration treatment enhanced the removal capacity of both concentration levels ( $P < 0.001$  at 2.5 mg/l and  $P < 0.029$  at 10 mg/l). In the second trial, comparing phillipsite and clinoptilolite starting at 10 mg/l ammonia, average adsorption was at least 57% of initial concentration. ANOVA of final adsorption showed no differences between natural phillipsite and clinoptilolite. Although not significantly different at the 5% level ( $P \leq 0.069$ ),  $\text{NH}_4^+$  final concentration was constantly lower for phillipsite than for clinoptilolite ( $4.45 \text{ mg/l} \pm 0.21$  vs.  $4.95 \text{ mg/l} \pm 0.06$ ).

Regeneration with three bed volumes of NaCl 1M after first use gave similar final concentrations ( $4.67 \text{ mg/l} \pm 0.10$  vs.  $4.60 \text{ mg/l} \pm 0.73$ ), probably because ion exchange between the zeolite-linked  $\text{K}^+$  and the  $\text{Na}^+$  of the regenerating solution maximized the ammonia exchange capacity of the tested tuffs, and in particular phillipsite which is rich in  $\text{K}^+$  (Vaughan 1978).

The same regenerating treatment, operated on exhausted (entirely ammonia-exchanged)

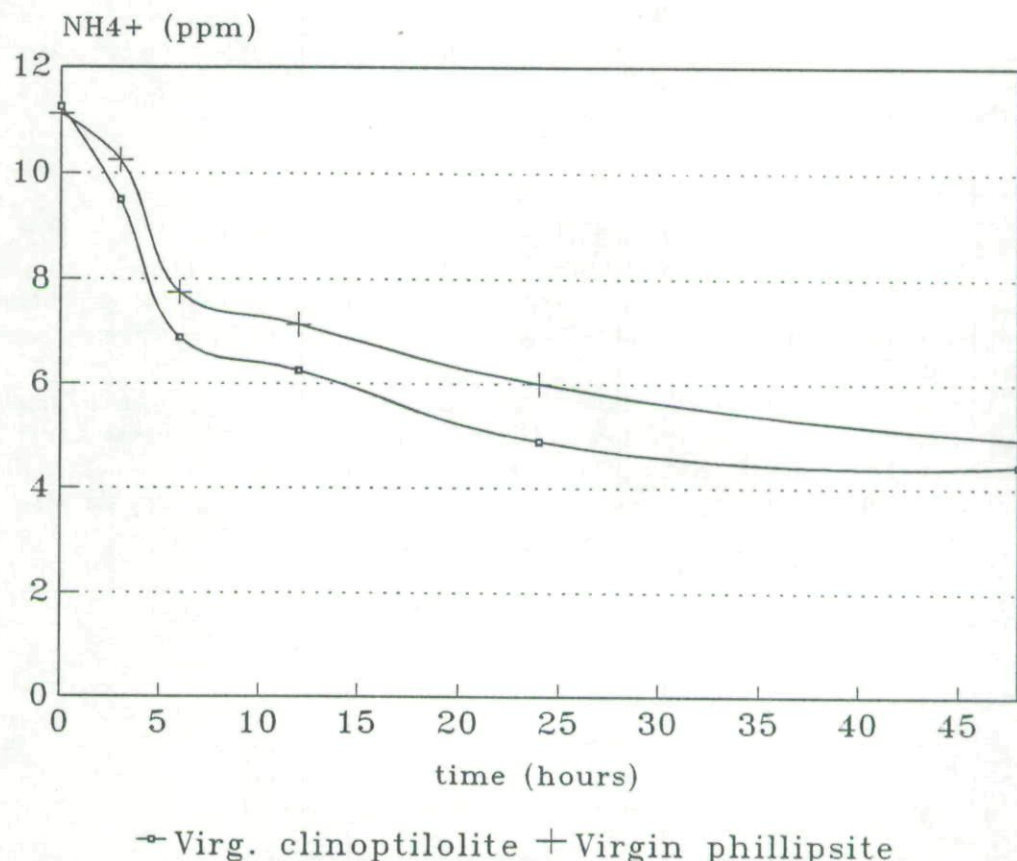


Figure 1. Ammonia adsorption, initial concentration 10 ppm; phillipsite vs. clinoptilolite.



phillipsite and clinoptilolite, did not recover the original efficacy. However, clinoptilolite showed better results (final concentrations:  $6.17 \text{ mg/l} \pm 0.10$  vs.  $6.67 \text{ mg/l} \pm 0.13$ ); this zeolite, in effect, has a worse  $\text{NH}_4^+$  selectivity than phillipsite (Sherman 1978), as framework-linked ammonia is more easily exchanged.

The number of bed volumes for regeneration was chosen according to Lopez & Liberti (1991). Ten bed volumes of regenerating solution allowed the initial efficacy of exhausted clinoptilolite and phillipsite to recover (average adsorption was  $43.60\% \pm 4.64$  and  $42.45\% \pm 2.05$ , respectively). In the same conditions, 24 bed volumes were needed to improve the original ion exchange power. In these conditions phillipsite gave better results than clinoptilolite for final adsorption ( $P \leq 0.051$ ) and final concentrations as  $\text{mg/l}$  ( $2.32 \pm 0.09$  vs.  $2.02 \pm 0.28$  and  $P \leq 0.052$ ). These results are interesting, even if the 5% probability level was slightly exceeded. Trends of ammonia concentration in this trial are shown in Figs 1, 2 and 3.

In ammonia-increasing concentration trials, clinoptilolite and phillipsite showed similar efficacy. Regenerated zeolites, however, had better effectiveness than natural ones. Virgin and regenerated phillipsites seem to be saturated more slowly than clinoptilolite.

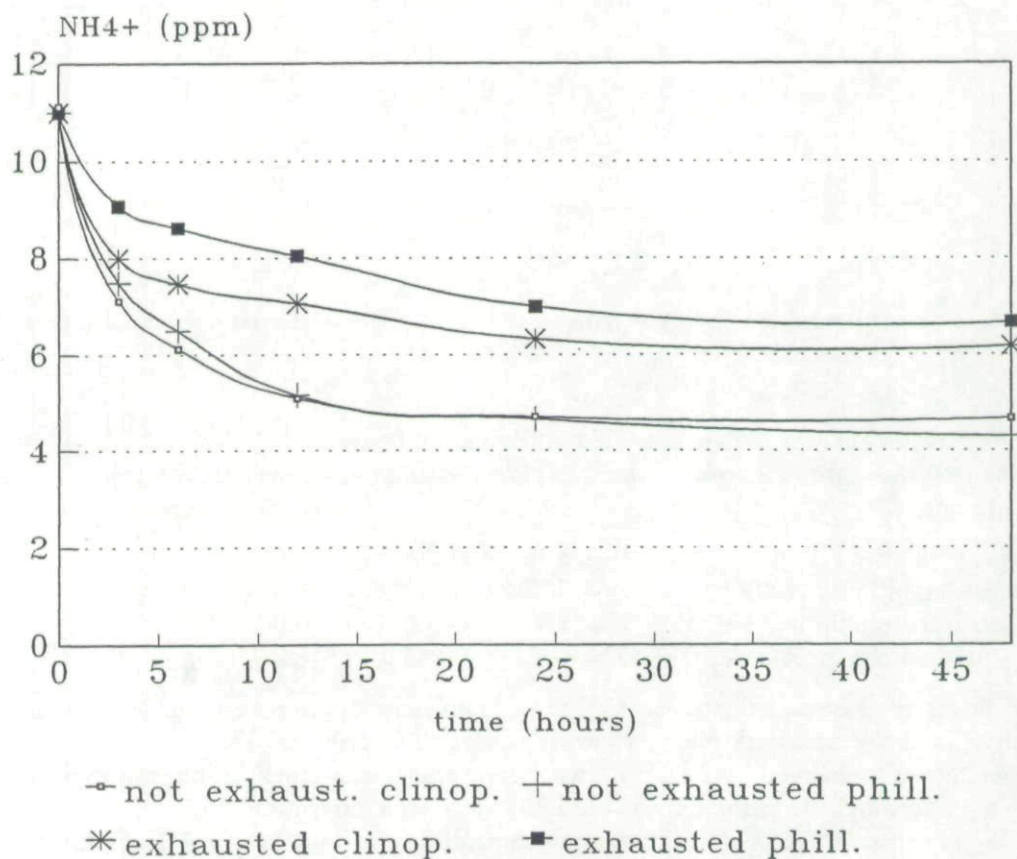


Figure 2. Ammonia adsorption, initial concentration 10 ppm; phillipsite and clinoptilolite, exhausted or not exhausted materials regenerated by three bed volumes.

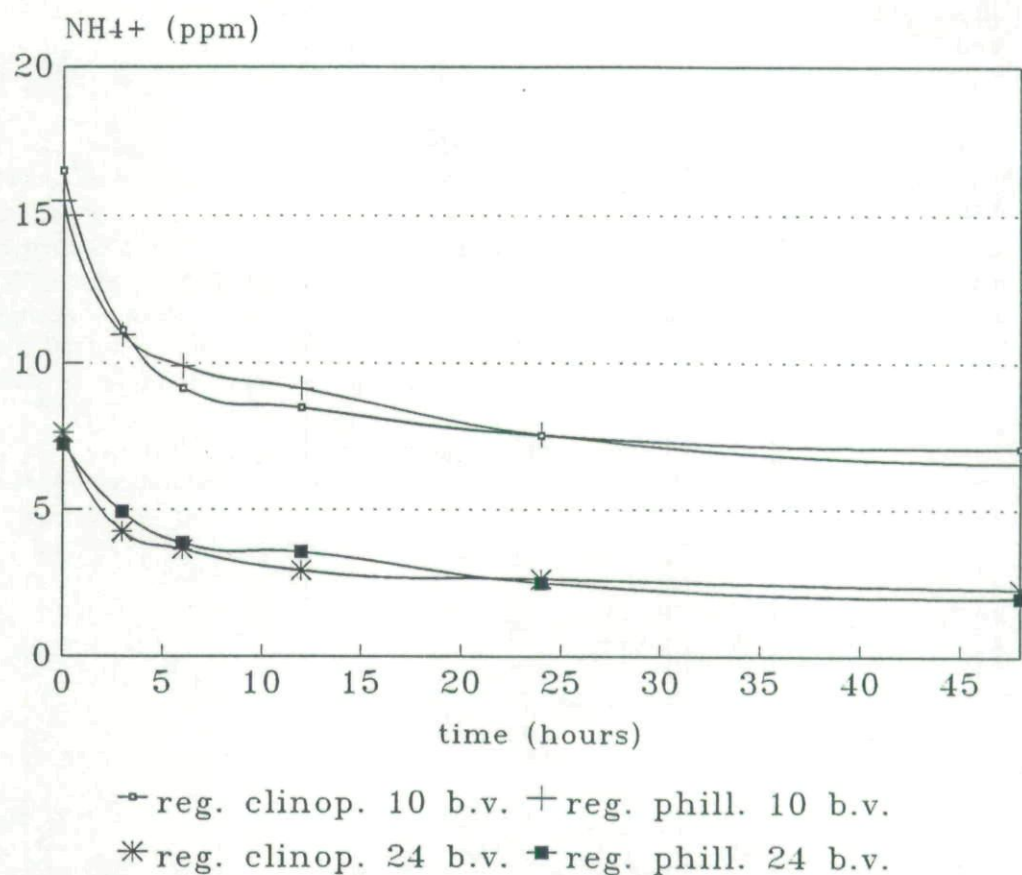


Figure 3. Ammonia adsorption, initial concentration 10 ppm; phillipsite vs. clinoptilolite, exhausted materials regenerated by 10 or 24 bed volumes.

Regression analysis of data collected in the period between the third and the 14th day of the trial showed the following trends, where  $Y$  is ammonia concentration (ppm) and  $X$  is trial time (days):

Virgin phillipsite (100 g):	$Y = 5.188 + 0.936 X, r^2 = 0.98$
Virgin clinoptilolite (100 g):	$Y = 5.074 + 0.917 X, r^2 = 0.96$
Regenerated phillipsite (100 g):	$Y = 3.912 + 0.567 X, r^2 = 0.97$
Regenerated clinoptilolite (100 g):	$Y = 4.653 + 0.865 X, r^2 = 0.95$

The linear regressions are shown in Fig. 4. Trout-rearing trials were carried out using zeolites in closed and dark filters, to avoid confounding effects.

Ammonia exchanged by phillipsite was, on average, one-third of total fish excretion:  $8.1 \mu\text{g/g}$  live weight/h ammonia was found in the recirculating water.

In the second stage of the trial ammonia excretion was found to be  $4.3 \mu\text{g/g}$  l.w./h in fasting conditions, and  $12.4 \mu\text{g/g}$  l.w./h when fed 1.2% wet weight of a commercial diet containing 47% crude protein.

In the last trial, weight gain and feed conversion ratios of 100 g trout fed 1.2% wet



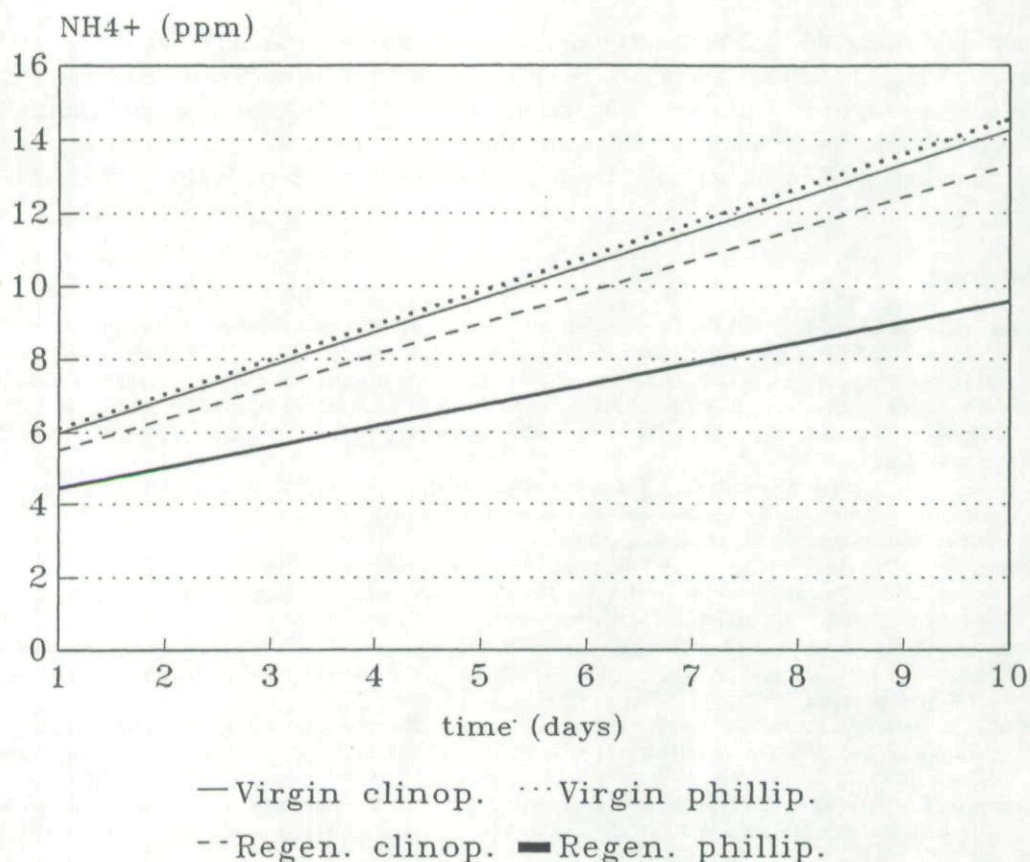


Figure 4. Rise of ammonia concentration, 100 g virgin and regenerated materials.

weight were monitored at 4 and 6 kg/m<sup>3</sup> stocking densities. Again ammonia removal was good at 4 kg/m<sup>3</sup>; regression analysis showed the following trend of ammonia concentration against time:

Stocking density 4 kg/m<sup>3</sup>:  $Y = 1.972 + 0.719 X$ ,  $r^2 = 0.97$

Stocking density 6 kg/m<sup>3</sup>:  $Y = 2.27 + 1.813 X$ ,  $r^2 = 0.99$

### Conclusions

The use of zeolites, and in particular of phillipsite and clinoptilolite, in intensive aquaculture systems seems promising, not only for their efficiency in NH<sub>4</sub><sup>+</sup> removal, but also as regards the cost; zeolitic tuffs are much cheaper than other materials. The phillipsite and clinoptilolite tuffs tested have similar efficacy when freshly used, but NaCl-exchanged phillipsite shows a greater effectiveness.

NaCl-operated regeneration improves ion exchange capacity of all the tested zeolites, but virgin phillipsite and clinoptilolite were particularly effective in ammonia removal from aquaculture waste water. It would be possible to use zeolite as natural material,



replacing exhausted tuffs with new ones, or to re-use the same material with periodic regenerations. In neither case are there environmental problems. Exhausted zeolites can be used as nitrogen fertilizers in agriculture (Passaglia 1991), or ammonia-exchanged NaCl solution can be purified, obtaining  $\text{MgNH}_4\text{PO}_4$ , once again utilizable as a high premium-quality slow-release solid fertilizer (Amicarelli & Liberti 1991).

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