(28)

Pergamon

Wat. Sci. Tech. Vol. 35. No. 7, pp. 47–54, 1997.

0273–1223/97 $17·00 + 0·00

PII: S0273-1223(97)00113-3

PERFORMANCE OF CLINOPTILOLITE ALONE AND IN COMBINATION WITH SAND FILTERS FOR THE REMOVAL OF AMMONIA PEAKS FROM DOMESTIC WASTEWATER

Bilsen Beler Baykal and Didem Akca Guven

Istanbul Technical University, Department of Environmental Engineering, 80626 Ayazaga, Istanbul, Turkey

ABSTRACT

Ion exchange using clinoptilolite for the removal of peak concentrations of ammonia from domestic wastewater as a second stage, by itself and in combination with sand filters, is evaluated. It is observed that there is no significant loss of capacity of clinoptilolite when placed in sand filters. All three configurations studied are successful in the removal of peak concentrations of ammonia, and hence can be used as a polishing unit, to comply with the demands of stringent standards. Among those investigated, the combined scheme, with clinoptilolite and aerated sand filters where biological activity is enhanced, is found to be the most effective provided that sufficient time for the development of nitrifiers are allowed. The performance loss of the clinoptilolite was observed to be 10% after 10 cycles of regular operation and regeneration. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Ammonia removal; clinoptilolite; ion exchange; multipurpose filters; peak loads; sand filters.

INTRODUCTION

With increasing quantities of pollutants being discharged into receiving waters over the years, new and more stringent effluent quality standards have been adopted in various countries of the world. One of these pollutants is ammonia with its well known consequence of eutrophication in water resources with insufficient circulation.

The classical solution to the problem of ammonia removal is biological treatment and research devoted to various aspects of nitrification/denitrification is numerous. These processes are very effective in nitrogen removal, however, when exposed to peak and variable loads, they may fall short in removing the influent concentration patterns and fail to achieve the required effluent quality. A polishing unit or an upgrade may be needed to comply with stringent standards like those given for "sensitive areas" as described by the European Community.

An alternative to these biological treatment processes is the physicochemical process of ion exchange with an ion exchanger that is highly selective for ammonia. It has been demonstrated that clinoptilolite is very effective in the removal of ammonia, and in the equalization of ammonia peaks. Previous work on the removal of ammonia by clinoptilolite has been presented by Weber (1972), Koon and Kaufman (1975), Czaran (1988) and Beler Baykal *et al.* (1994, 1996). As such, the use of a clinoptilolite unit would be a very good tool for compliance with stringent standards of ammonia or alternatively total inorganic nitrogen. Such a unit may be used as an upgrade in existing systems as well as in new treatment plant designs.

Beler Baykal *et al.* (1994, 1996) have also demonstrated that clinoptilolite is very effective in the removal of ammonia peaks in laboratory scale experiments of 60 cm columns; and Oldenburg and Sekoulov (1995) have shown its use in larger scale columns of 4.2 meters, by itself and in combination with filters of 4 mm diameter burned clay. Beler Baykal *et al.* (1994, 1996) have further pointed at the insufficiency of a biological system of a fixed bed of nitrifiers to dampen peak loads of ammonia when exposed to peak concentrations in the influent. Under such circumstances, the influent peak pattern is repeated in the effluent, as depicted in Figure 1.

After the success of the systems described above, the need to assess the capacity of using clinoptilolite in combination with sand filters, which are much more commonly used in filtration as compared to burned clay, arose. The present work was undertaken in an effort to evaluate the performance of clinoptilolite in combination with sand filters. Within its scope, the possibility of using clinoptilolite alone and in combination with various configurations of sand filters to remove ammonia from domestic wastewater was investigated, with specific emphasis on the removal of peak concentrations. As such, the system was mainly intended as a second stage/polishing unit after some nitrification scheme. During peak loads where the rate of incoming ammonia exceeds that of removal through nitrification, the ion exchange process takes over and the ion exchange capacity provided works to eliminate peaks in the effluent. The following configurations were used within the context of this work: (i) Clinoptilolite only, (ii) Clinoptilolite in combination with a sand filter, (iii) Clinoptilolite in combination with a sand filter enriched with biological activity. The performance of clinoptilolite after various cycles of regular operation and regeneration was also investigated to evaluate the capacity of the ion exchanger. A comparison of a combination of clinoptilolite and filter material, namely sand, with and without aeration is also presented.

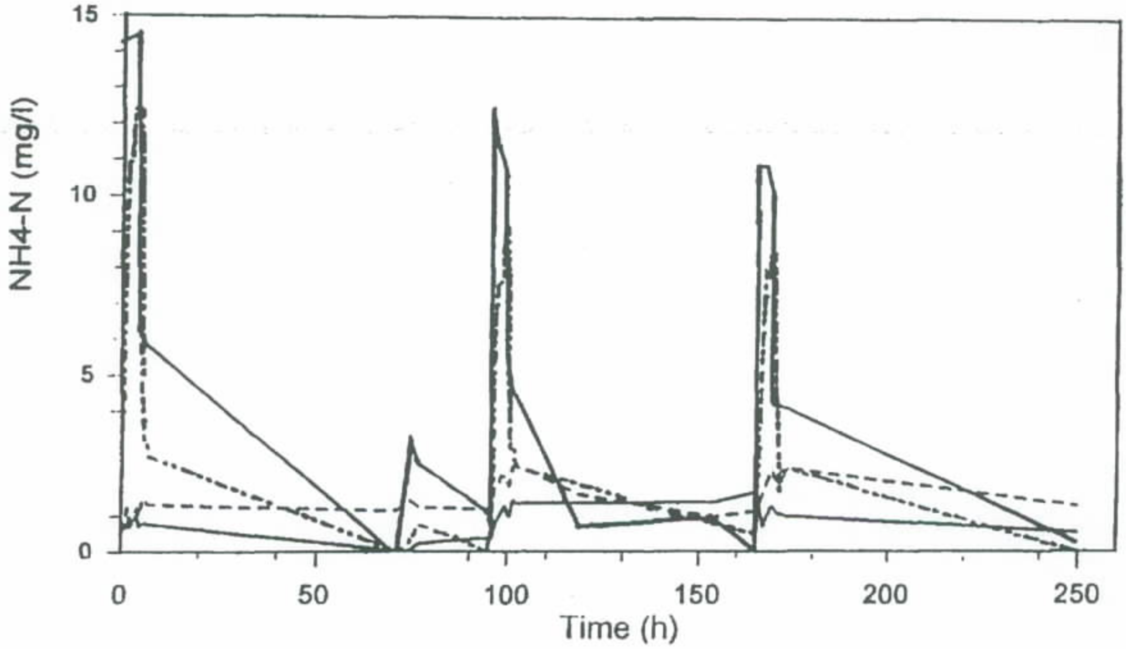


Figure 1. Response of clinoptilolite only, fixed bed of nitrifiers on burned clay filter material only, and the combined scheme (Beler Baykal *et al.*, 1996)

EXPERIMENTAL WORK

Within the scope of this work, the capability of clinoptilolite alone and in combination with sand filters was evaluated for ammonia removal from domestic wastewater with specific emphasis on dampening of peak concentrations of ammonia.

In the experiments, the sodium form of the clinoptilolite from the Beli Plast region of Bulgaria was used. The typical composition is given as 65.90% SiO_2, 12.97% Al_2O_3, 4.93% K_2O, 2.30% CaO, 2.12% Na_2O, and less than 1% ferric, magnesium and titanium oxides (Gradev, 1973). The filter material used in the columns was sand of the particle size range of 2.0 to 2.3 millimetres.

Three different configurations were investigated within the context of this work:

(i) Clinoptilolite only
(ii) Clinoptilolite combined with a sand filter
(iii) Clinoptilolite combined with a sand filter in which biological activity was enhanced through aeration and pH control.

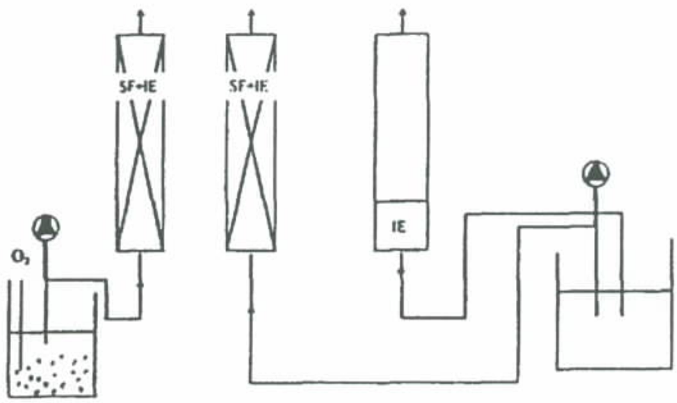
Experiments were all performed in columns of 2.6 cm diameter and 60 cm. of height, in the upflow mode. The basic experimental setup is presented in Figure 2 and Table 1.

The feed was provided from the domestic wastewater discharge line of Istanbul Technical University and was aerated, filtered and the concentration was fixed at the prescribed value by the addition of ammonium chloride or tap water, to represent an effluent from a biological treatment plant in terms of ammonia. Analysis of ammonia was conducted through the use of an ion meter and an ammonia electrode.

The experiments were undertaken in three phases:

(i) Fundamental analyses,
(ii) Investigation of performance under peak concentrations of ammonia,
(iii) Investigation of performance after regeneration.

First, fundamental investigations on the removal of ammonia were performed through breakthrough analyses in an effort to determine appropriate operating conditions like contact time, surface loading and water velocity.



SF: Sand Filter, IE: Ion Exchanger

Figure 2. The experimental setup.

Table 1. Characteristics of the experimental system

Water velocity	1 m/h
Water flowrate	10 ml/min.
Packed height	
Column A and B	58 cm.
Column C	8.5 cm.
Ion exchanger	
Type	Clinoptilolite
Mass	40 g
Size range	1-2 mm.
Equivalent diameter	1.19 mm.
Filter material	
Type	Sand
Size range	2-2.3 mm.
Equivalent diameter	2 mm.

The influent concentrations used were 15-17 mg NH_3-N/l. In this phase, the effect of placing clinoptilolite in a bed of sand was also investigated through further breakthrough analyses. Then, peak loads of ammonia were introduced. The systems were operated for 10 days non-stop, receiving one 4-hour peak of 2 to 5 times the average concentration of ammonia, which was 3 to 5 mg/l, per day. Finally, two breakthrough curves were prepared to compare a sample of fresh, unused clinoptilolite in the sodium form with another sample which had been used and regenerated 10 times.

RESULTS AND DISCUSSION

Within the scope of this work, three phases of experiments were conducted: (i) those that were directed towards fundamental analyses of the various configurations described, (ii) those that were intended for peak concentrations, and (iii) those that were undertaken to evaluate performance after some regeneration.

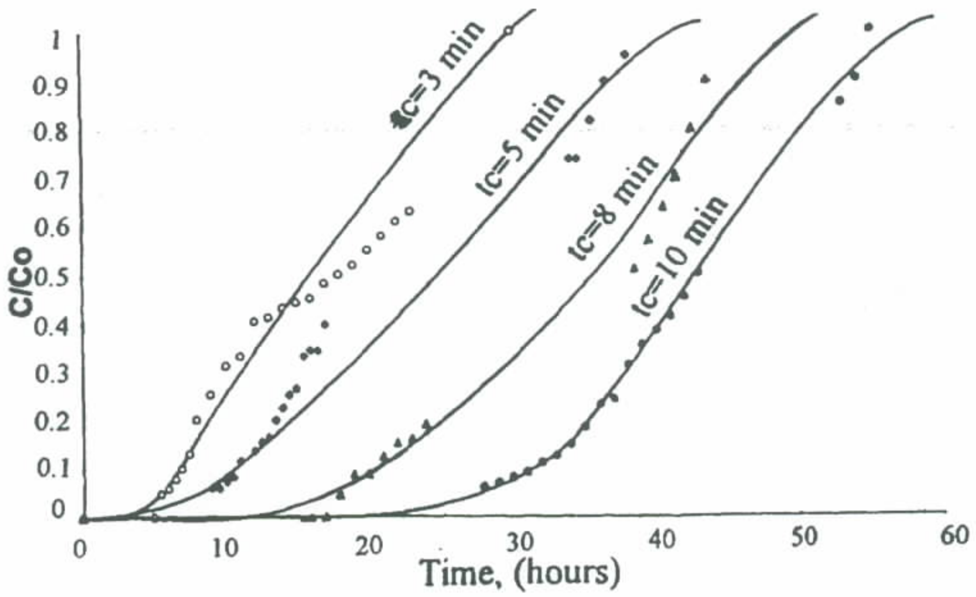


Figure 3. Breakthrough analyses for clinoptilolite.

Fundamental analyses

First, a breakthrough analysis of a column of clinoptilolite only, with a diameter of 2.6 centimetres and 40 grams of clinoptilolite, was run to determine the capacity of ion exchange and fundamental process variables for subsequent runs, like water velocity and contact time. Water velocity was varied between 1.6 and 0.5 metres per hour corresponding to contact times between 3 to 10 minutes, in accordance with the recommendations of Beler Baykal *et al.* (1996). Figure 3 depicting the results of those runs, confirms that any contact time within the range studied may be used. As expected, time to reach breakthrough increases as contact time is increased, and using a high contact time would be beneficial in terms of extended service time. However, as indicated in Table 2, the range studied corresponds to a surface loading range of 0.009-0.01m^3/m^2.min which is quite low as compared to the typical surface loading rates of 0.08-0.4 m^3/m^2.min. Five minutes contact time was used for further investigations undertaken within the scope of this work. The capacity of the clinoptilolite at this contact time was calculated to be 3.6 mg ammonia nitrogen per gram of clinoptilolite at an influent concentration of 15 mg ammonia nitrogen per litre. In the next stage, two other configurations (i) a combination of sand and clinoptilolite of 14% by volume, and (ii) a combination of sand and clinoptilolite of 14% by volume, which was aerated to enhance biological activity, were added to the column that contained clinoptilolite only.

Table 2. The capacity of clinoptilolite at different contact times and surface loadings

Contact time (min.)	Surface loading (m^3/m^2.min)	Capacity used (mg NH_4-N/g clino.)
3	0.030	2.8
5	0.020	3.6
8	0.010	2.0
10	0.009	2.2

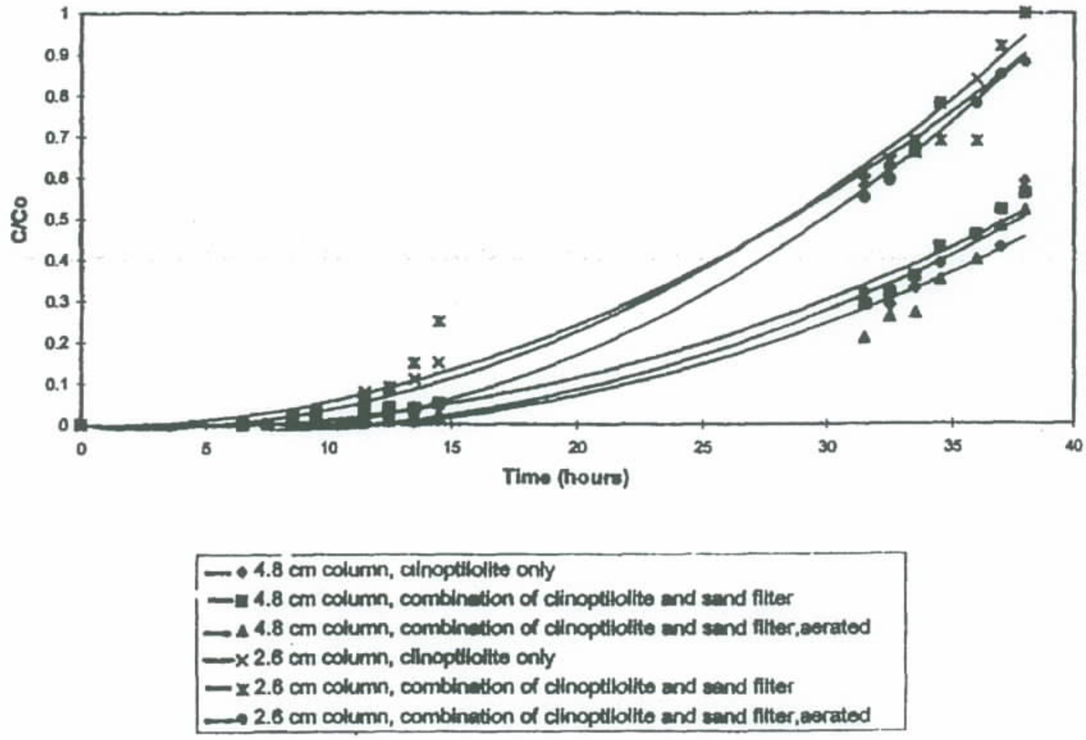


Figure 4. Breakthrough curves at a contact time of five minutes.

The three columns were operated in a parallel mode receiving the same feed. Breakthrough curves shown in Figure 4 were generated to compare the three columns, especially to detect any discrepancies due to the placement of the ion exchanger in the filter bed, like a probable loss of some capacity. Figure 4 reveals that wherever the clinoptilolite is used, by itself or in a filter bed, its performance in terms of removal of ammonia is compatible. Figure 4 also presents a comparison of the performance of the columns as the amount of clinoptilolite is doubled, i.e. 80 grams, and the column diameter is increased to 4.8 centimetres. About a two-fold increase in the performance is achieved by doubling the amount of the ion exchanger.

Performance under peak concentrations of ammonia

After the fundamental investigations described above, peak loads of ammonia were introduced into the three columns working in parallel. Starting from fresh clinoptilolite, the columns were operated for ten days non-stop, receiving one four-hour peak, of two to five times the average concentration of ammonia, per day. Figure 5 presents the results of those experiments, revealing that removal of ammonia reaches 100% at the very beginning for all columns. This is a good indication confirming the ability of all three configurations investigated, clinoptilolite by itself or integrated in sand filters, in terms of dampening influent peak concentrations of ammonia.

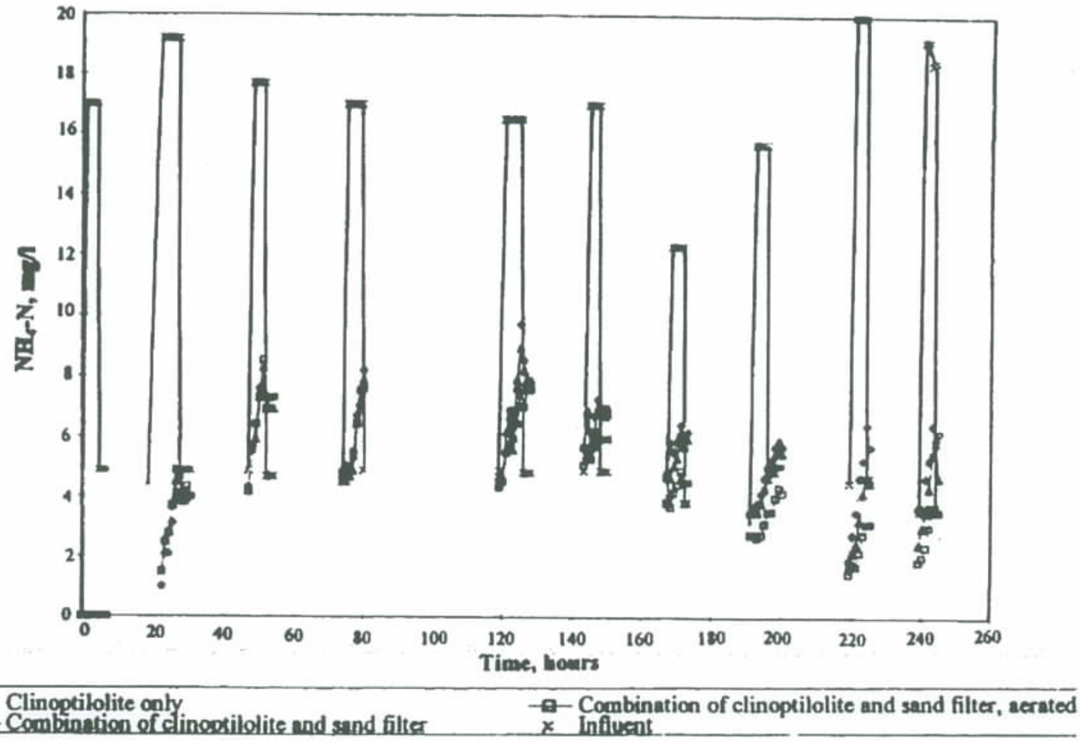


Figure 5. Response to peak concentrations of ammonia.

The results indicated further that the configuration with enhanced biological activity, where ammonia is removed not only by ion exchange, but also by the additional nitrification capacity provided by the biofilm produced within the filter, becomes more and more beneficial as time passes, owing to the adaptation of the nitrifiers and their improving action on the removal of ammonia. In this configuration, at low influent concentrations of ammonia, desorption occurs, and the desorbed ammonia is in turn consumed in the process of nitrification provided within the same column. At the end of 10 days of non-stop operation, the column with biological activity removes 77% while the one with clinoptilolite removes 61%. This is also an indication of partial regeneration in the column with biological activity.

The results from these two phases have indicated that the use of clinoptilolite in sand filters will provide benefits of improving the effluent quality in terms of ammonia. This practice may be a useful tool in older plants with sand filters, in the form of an upgrade by replacing a part of the filter material by clinoptilolite, where an ion exchange feature to remove ammonia is added; or alternatively aerating this system to enhance nitrification along with ion exchange. The system also gives an alternative for a well polished effluent in terms of ammonia in the design of new plants. As such, the system will be employed as a multipurpose filter.

Performance after regeneration

Finally, two breakthrough curves, one for fresh clinoptilolite and another with clinoptilolite which had been used in regular operation and regenerated within ten cycles, were generated in an effort to evaluate the performance of the ion exchanger after various regenerations. The results presented in Figure 6, reveal that there is a loss of capacity of 10% after ten regenerations with a solution of one molar sodium chloride solution at a pH around 8.

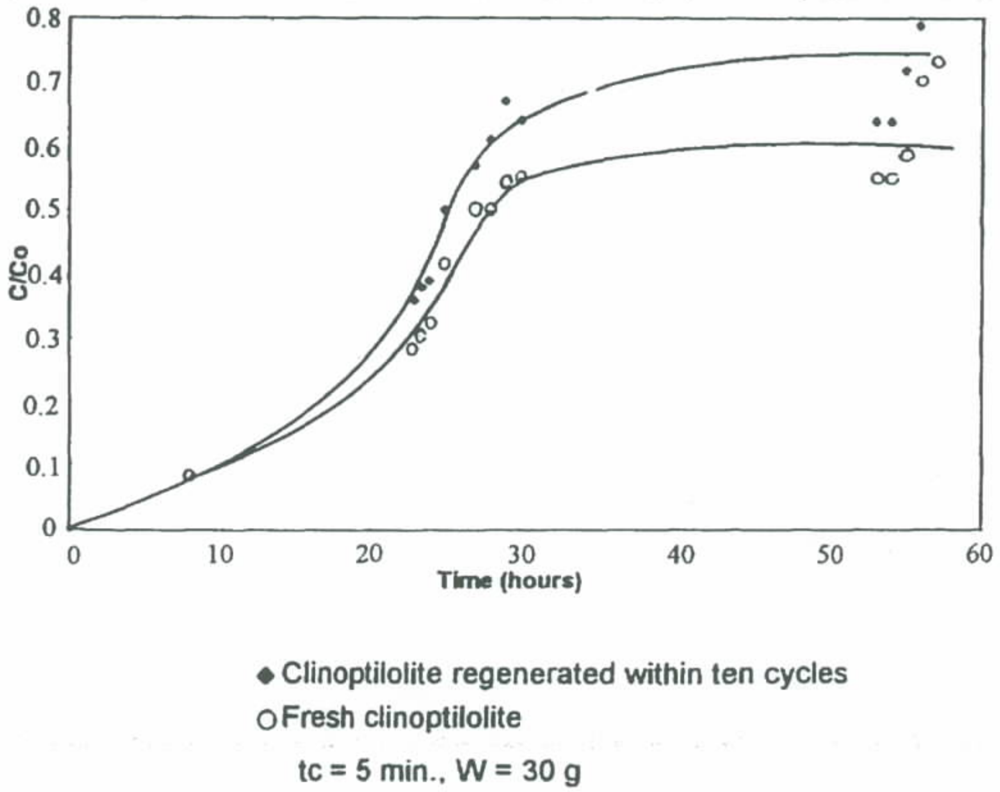


Figure 6. The effect of regeneration on the performance of clinoptilolite.

As indicated earlier, there is the benefit of partial biological regeneration in the sand filter with clinoptilolite where biological activity is enhanced. However, the results indicate that it will not be sufficient to abandon the need for chemical regeneration.

CONCLUSIONS

The results have revealed that the integration of clinoptilolite in sand filters is possible without losing its effectiveness. This is a very good indication of a promising revision in the form of replacing a part of the filter material that is intended for the removal of suspended solids with clinoptilolite to get additional benefits of ammonia removal for those plants which already have sand filters. Under those circumstances, the unit will be used as a multipurpose filter.

Comparison of the results from the combined systems and clinoptilolite only have revealed that all configurations are effective in the removal of influent ammonia peaks. At the beginning, the performances of all three are comparable at around 100%. The results indicate further that the configuration with biological activity becomes more and more beneficial as time passes owing to the adaptation of the nitrifiers.

At the end of 10 days of non-stop operation, the column with biological activity removes 77% while the one with clinoptilolite removes 61%. Also an evidence of partial regeneration in the column with biological activity was observed. However, its extent is not sufficient to abandon chemical regeneration completely, under the experimental conditions employed in this work. Finally, the loss of capacity of clinoptilolite after 10 regenerations was observed to be 10%.

REFERENCES

Beler Baykal, B., Oldenburg, M. and Sekoulov, I. (1994). Post equalization of ammonia peaks. *Water Research*, **28**(9), 2039-2042.

Beler Baykal, B., Oldenburg, M. and Sekoulov, I. (1996). The use of ion exchange in ammonia removal under constant and variable loads. *Environmental Technology*, **17**, 717-726.

Czaran, E., Meszaros-Kis, A. and Domokos, E. (1988). Separation of ammonia from wastewater using clinoptilolite as ion exchanger. *Nuclear and Chemical Waste Management*, **8**, 107-113.

Gradev, G., Sekoulov, I., Oldenburg, M. and Gulyas, H. (1993). Exchange of ammonium on clinoptilolite and its application in sewage-wastewater purification. *Zeolite 93, 4th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites*, Idaho, USA.

Koon, J. H. and Kaufman, W. J. (1975). Ammonia removal from municipal wastewaters by ion exchange. *Journal of Water Pollution Control Federation* **47**(3), 448-465.

Oldenburg, M. and Sekoulov, I. (1995). Multipurpose filters with ion exchanger for the equalization of ammonia peaks. *Wat. Sci. Tech.*, **32**(7), 199-206.

Weber, W. J. (1972). *Physicochemical Processes for Water Quality Control*, Wiley-Interscience, U.S.A.