Bioregenerated ion-exchange process: The effect of the biofilm on the ion-exchange capacity and kinetics

Ori Lahav and Michal Green*
Faculty of Agricultural Engineering, Technion, Haifa 32000, Israel

Abstract

A new process for ammonium removal from wastewater using zeolite has been developed. The zeolite (chabazite) serves the dual purpose of an ion exchanger and a physical carrier for nitrifying bacteria which bio-regenerate the ammonium-saturated mineral. The entire process is carried out in a single, compact reactor and takes place in two phases: ion-exchange phase and bioregeneration phase.

This paper describes the effects of the biofilm on ion-exchange capacity and kinetics. Batch and continuous experiments showed a reduction of about 25 to 30% in the ion-exchange rate in biofilm covered chabazite as compared to virgin chabazite, while the ion-exchange capacity did not change. Experiments conducted indicated that the rate-controlling step for ion exchange shifted from pore diffusion in the virgin chabazite to film diffusion in the biofilm-covered chabazite. The diffusion rate of NH_4^+ inside biofilms is of the same order of magnitude as diffusion rate of NH_4^+ in water and 3 to 4 orders of magnitude greater than typical pore diffusion rates reported in zeolites. Therefore, the biofilm coverage of the chabazite was originally not expected to affect the ion-exchange rate. In addition, chemical precipitation was experimentally found not to be the cause for the ion-exchange rate reduction.

It was hypothesised that the rate-limiting factor for ion exchange was caused by the part of the biofilm adjacent to the chabazite which differs from the rest of the biofilm and is characterised by a much higher density which impedes diffusion.

Introduction

A new process for ammonium removal from wastewater has been developed at the Technion. The process uses chabazite, an ion-exchange mineral of the zeolite group, to remove ammonium from wastewater effluents. The zeolite also serves the dual purpose of a physical carrier for nitrifying bacteria which bio-regenerate the ammonium-saturated mineral. By removing the nitrogen from the whole treatment plant flow, a more efficient and flexible wastewater treatment scheme is facilitated. The process has the advantages of the ion-exchange process (high reaction rate, good control of effluent quality, no sensitivity to fluctuations in NH_4^+ influent concentrations), while overcoming its main drawback, the costs involved in the chemical regeneration by employing biological regeneration of the ion exchanger.

The process is carried out in a single, compact reactor and takes place in two phases:

Ion-exchange mode (NH_4^+ separation stage): A column filled with zeolite (chabazite) is used for ammonium ion exchange from secondary or primary effluents. When NH_4^+ concentration breakthrough occurs the system switches to the bioregeneration mode.

Bioregeneration mode (nitrification stage): The same column containing the ammonium-rich chabazite is used during the bioregeneration mode as a fluidised bed reactor for biological nitrification with the chabazite acting as the carrier for the biofilm. A cation containing regenerant solution is recirculated through the bed in order to desorb NH_4^+. The amount of the NH_4^+ desorbed and its concentration in the regenerant solution is a function of the total cation concentration in the solution and the recirculated solution volume. After a short time, the solution reaches an apparent equilibrium concentration of ammonium (Reaction I), while simultaneously, the biomass starts to oxidise ammonia (Reaction II).

I. desorption: $Z - NH_4^+ + Na^+ \leftrightarrow Z - Na^+ + NH_4^+$
II. nitrification: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$

The oxidation of the liberated ammonia to the nitrate anion in the second reaction, shifts the equilibrium in the first reaction to the right and desorption continues until the ammonium concentration in the solution drops to negligible values. At this point, the amount of NH_4^+ remaining in the chabazite to the next adsorption phase is a function of the cation composition and concentration of the recirculated regenerant solution.

During the regeneration mode, the reactor operates in an almost batch mode (no outflow and minimal inflow) and pressurised oxygen is supplied for the nitrification process together with bicarbonate to maintain constant pH. The oxidation of the desorbed ammonium to nitrate anions allows for the reuse of the regenerant during many cycles of nitrification. The addition of external cations is limited only to the amount of sodium bicarbonate buffer added. At the end of both adsorption and regeneration modes, backwash is practiced. After the adsorption mode, backwash removes suspended solids thus preventing bed clogging and heterotroph bacteria accumulation in the bed which might compete with the nitrifier population. At the end of the bioregeneration mode, backwash removes the remaining regenerant solution from the bed which may deteriorate ion exchange efficiency at the beginning of the next adsorption phase. This nitrate-rich backwash water is considered a product rather than a pollutant and therefore denitrification is not necessary. A schematic description of the system is shown in Fig. 1.

Results from experiments with either simulated, secondary, or primary effluents showed that the process is capable of high-rate ammonium removal and stable performance (an average nitrification rate of 7.2 g NH_4-N/(ℓ reactor·d) was obtained during the

* To whom all correspondence should be addressed.
☎+972-4-829 3479; fax +972-4-829 2606;
e-mail: agmgreen@techunix.technion.ac.il
Received 7 January 1999; accepted in revised form 7 October 1999.

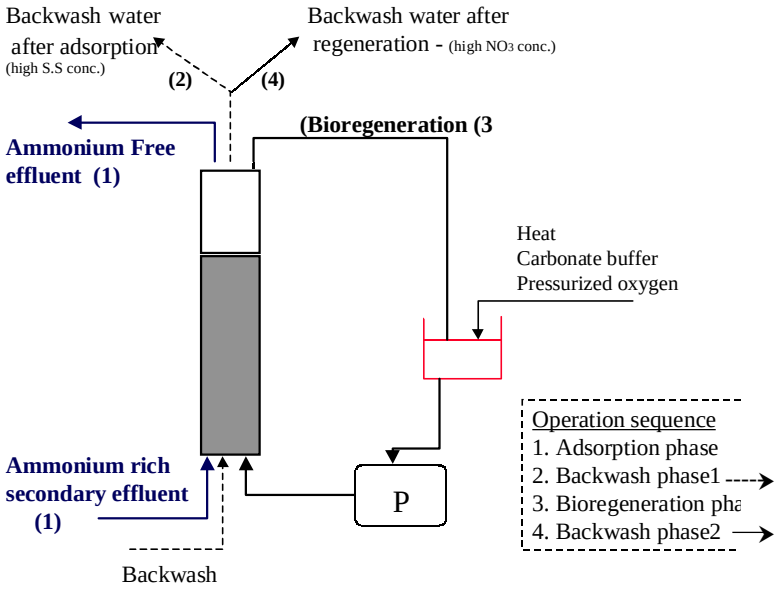

Figure 1
Schematic representation of the process

bioregeneration mode). A high nitrifying population was established with only minimal heterothrophic bacterial competition. Moreover, the system was found not to be sensitive to bed clogging even when actual secondary and primary effluents were treated. Detailed description of the process is given elsewhere (Green et al., 1996; Lahav and Green, 1998).

However, side experiments carried out on the biofilm covered chabazite showed a reduction of up to 30% in the number of bed volumes (BV) to ammonium breakthrough (in comparison to virgin chabazite), indicating a deterioration in ion-exchange kinetics or/and capacity.

In the described process the ion-exchanger particles act as a carrier for the biomass, i.e. the particles are covered by biofilm. Average biomass concentrations varied between 2.0 mg proteins/g chabazite when air was used in the bioregeneration phase and 8.5 mg proteins/g chabazite when pure oxygen was used. Accordingly, nitrification rates varied between 1.0 g N/ℓ reactor·d to 7.2 g N/ℓ reactor·d.

Information regarding the effects of biofilm covering ion-exchange material on the ion-exchange characteristics is scarce. This is probably because the accumulation of biomass on ion-exchange particles in classical ion-exchange processes is minimal. However, reduction in adsorption efficiency caused by biofilm coverage has been reported in biological activated carbon processes. Bishop et al. (1972) reported that biological growth on activated carbon beads caused a drop in adsorption efficiencies from approximately 75% to 80% to approximately 55%. Flynn et al. (1976) report that about 30% of the surface of carbon that had been in contact with bacteria for an average of 5 d was inaccessible for adsorption. Lowry and Burkhead (1980) reported that the adsorptive capacity of GAC (granulated activated carbon) diminished rapidly with the establishment of even a very light coating of biological solids. In contrast, Nakhla and Suidan (1995) found that the adsorptive capacity of activated carbon was not affected by the establishment of biofilm on the surface of the GAC granule. Shultz and Keinath (1984) reported reduced adsorption kinetics for phenol adsorption on biofilm-covered GAC granules. They concluded that the mass transfer through the biofilm had a significant effect on the rate of substrate removal by adsorption.

This paper concentrates on the effects of the biofilm coverage of the ion-exchange material on ion exchange capacity and on ion-exchange kinetics.

First, relevant information regarding ion-exchange kinetics, and transport rate of ions in biofilms, in relation to potential effects of the biofilm on the ion-exchange characteristics will be discussed. Results from experiments comparing ion-exchange characteristics of virgin and biofilm-covered chabazite will then be presented, and their relation to theoretical expectations, based on ion-exchange kinetics and ion transport rate in biofilms will be discussed.

Kinetics of ion exchange

Ion exchange is a diffusion process, the rate of which depends on the following relative rates:

- Transport of the exchanging ions in the bulk solution
- Transport of the exchanging ions through an adherent film (or boundary layer) at the particle surface - "film diffusion"
- Transport of the exchanging ions inside the particle pores- "pore diffusion"
- Actual rate of the ion-exchange process.

The rate of the ion exchange is determined by the slowest process. Only seldom does the actual ion exchange present the rate-limiting step for the ion-exchange process. Furthermore, the high flowrate typically practiced in water and wastewater treatment allows for relatively rapid transport of the ions in the bulk solution. Hence, film diffusion or pore diffusion are usually the rate controlling step. Film diffusion is a measure of the resistance to the transport of ions from the bulk solution through the hydrodynamic boundary layer or through a real surface barrier, if existing, to the outer surface of the ion-exchange particle. Film diffusion depends mainly on particle size, solution concentration, film thickness and the effective film-diffusion coefficient of the ions. In well-stirred conditions, the film diffusion coefficient is of the order of magnitude of 10^{-5} cm^2/s (Cherry, 1987). The film diffusion layer is a mathematical expression which depends on temperature, turbulence, and viscosity.

Pore diffusion relates to the ion diffusion rate within the exchange matrix. It is inversely proportional to the particle radius and directly proportional to the concentration of the fixed charges and the particle-diffusion coefficient, which depends on the intracrystalline structure of the zeolite.

In zeolites, pore diffusion is usually the rate-controlling step with reported values between 5×10^{-7} and 10^{-9} cm^2/s for Na^+, Cs^+, Sr^{2+} and Ce^{3+} and 4.2×10^{-7} or 6.8×10^{-8} cm^2/s for ammonia, depending on particle size (Dyer, 1988; Ames, 1965; Neveu et al, 1985). Film diffusion is the rate-controlling step in zeolites only at very low external cation concentrations (Dyer, 1988).

Transport of cations in biofilms

Cation diffusion coefficient in biofilms, with biofilm thickness ranging from a few microns to several hundred microns, varies from 20% to 95% of their corresponding value in water, i.e. of the

order of magnitude of 10^{-5} cm^2/s (Arvin and Kristensen, 1982; Wiliamson and McCarty, 1976; Characklis, 1990). The diffusion coefficient for ammonia in biofilm was found to be 80% of its value in water, about 1.3×10^{-5} cm^2/s (Wiliamson and McCarty, 1976). These values are of the same order of magnitude as those of typical film diffusion in stirred conditions. The much higher diffusion rates of the cations in biofilms, as compared to their pore diffusion rates (a difference of two to four orders of magnitude) indicate that the cations' transport rate through biofilm-covered ion-exchange particles should not affect the total ion-exchange process rate.

Materials and methods

Reactors

Columns with a working volume of 9.0 ℓ (8.3 cm diameter) filled with 2000 g chabazite zeolite were operated continuously for several months in alternate phases: 3 h in the ion-exchange mode, and 3 h in the bioregeneration mode. Biofilm concentration varied between 2.0 and 8.5 mg protein/g chabazite, which corresponds to about 2.0 and 8.5 gVSS/ℓ reactor. This variability was induced by changing the operating conditions (air vs. oxygen, loading rate).

Short-time continuous experiments which included breakthrough and 'interruption test' experiments were carried out in the reactors described above, by stopping the two-phase operation regime and conducting the specific experiment. Batch experiments were carried out in stirred 1 ℓ Erlenmeyer flasks containing either virgin or biofilm-covered chabazite particles originating from the continuous reactors.

Batch experiment procedures

Ion-exchange kinetics: Particles either virgin or biofilm-covered, were stirred in 250 mg/ℓ ammonium solution for a given time. At the end of that time the chabazite was taken out, washed with distilled water and regenerated in a 20 000 mg/ℓ Na^+ solution. Ammonium concentration in the solution after 24 h of regeneration was measured. This procedure was repeated for 6 different retention times: 10, 30, 60, 120, 240, and 420 or 600 min. This two-stage procedure was found to give better results than those obtained in the one-stage procedure due to minimisation of counter-ion competition and higher NH_4^+ measurement accuracy.

Total capacity: Either virgin or biofilm-covered chabazite samples were stirred in a 250 mg/ℓ NH_4^+-N solution for 24 h. The ammonia adsorbed during this period was then regenerated with a 20 000 mg/ℓ Na^+ solution for 24 h.

Breakthrough experiment procedures

Ammonium breakthrough experiments at different retention times were carried out on both virgin chabazite and biofilm-covered chabazite, with biofilm concentrations of 3.4, 6.6 and 8.4 mg protein/g chabazite (between 3.4 and 8.4 gVSS/ℓ - conversion based on chabazite packing density of approximately 500 g/ℓ and assuming 50% proteins of the total dry cell mass). The chabazite bed was chemically regenerated before each experiment using a 20 000 mg/ℓ NaCl solution (8 000 mg/ℓ as Na^+).This concentration was high enough to replace all other cations adsorbed to the chabazite in the continuous experiments. Higher concentrations were found to adversely affect the bacteria (Semmens and Porter, 1979).

Interruption tests

Interruption tests were used to identify the rate-limiting step - either film or pore diffusion (Kressman and Kitchener, 1949). Experiments were carried out in a 100 mℓ reactor filled with 60 g of either virgin chabazite or biofilm-covered chabazite (retention time = 90 s). For each chabazite sample two breakthrough tests were carried out: one continuous and the other with two 'interruptions'. During the interruption period, the chabazite was removed from the solution for 2 h.

The rate of diffusion after the chabazite column is put in contact with the solution after the 'interruption' should not be affected if film diffusion is the rate-controlling step. However, if pore diffusion is the rate-controlling step, the pause gives time to the concentration gradients inside the pores to level out. This will result in higher adsorption rate after the 'interruption' as compared to that prior to the interruption.

Feed solution

Simulated effluent with a typical Israeli sewage cation composition was used in the adsorption experiments. The cation composition is given in Table 1 (parentheses indicate the salt which was used).

TABLE 1
SIMULATED EFFLUENT SOLUTION USED IN THE EXPERIMENTS

Cation	Concentration
Na^+ ($NaCl$)	210-220 mg/ℓ
Ca^{++} ($CaCl_2.2H_2O$)	60 mg/ℓ
K^+ (KCl)	25 mg/ℓ
Mg^{++} ($MgCl_2.6H_2O$)	30 mg/ℓ
NH_4-N (NH_4Cl)	40 mg/ℓ

Specification of the chabazite

The zeolite used in all the experiments was a natural Herschelik-Sodium Chabazite (CABSORB-ZS500H) - Chabazite - distributed by GSA Resources Inc., Arizona, USA.

Chabazite specifications

Ion-exchange capacity:	2.8 meq/g
Packing density (dry):	0.58 g/cm^3
Pore space ratio:	0.37
Surface area:	521 m^2/g
Solid density:	1.73 g/cm^3

The chabazite was conditioned before use by alternating cycles of high concentrations of sodium and ammonium.

Analyses

NH_4^+ concentration was determined by the Phenate method (*Standard Methods*, 1992). Na^+ concentration was determined by ICP. The biomass concentration was measured by protein determination (Bradford, 1976).

Results and discussion

The effect of the biofilm on the ion-exchange rate and on total ion-exchange capacity

Batch experiments

Batch experiments were conducted on virgin chabazite and on chabazite covered with biofilm with a concentration of 8.4 mg protein/g chabazite (taken from a reactor operated for three months).

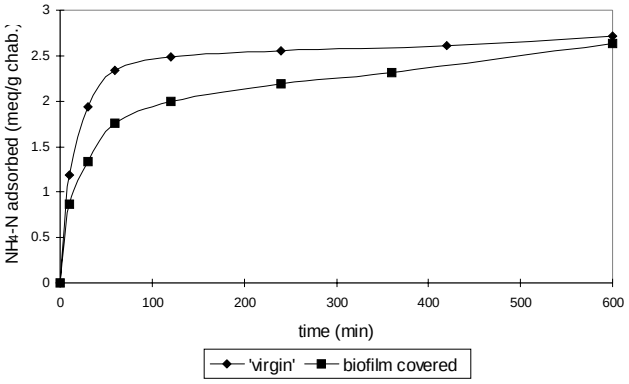

Figure 2
Adsorption kinetics of virgin and biofilm-covered chabazite

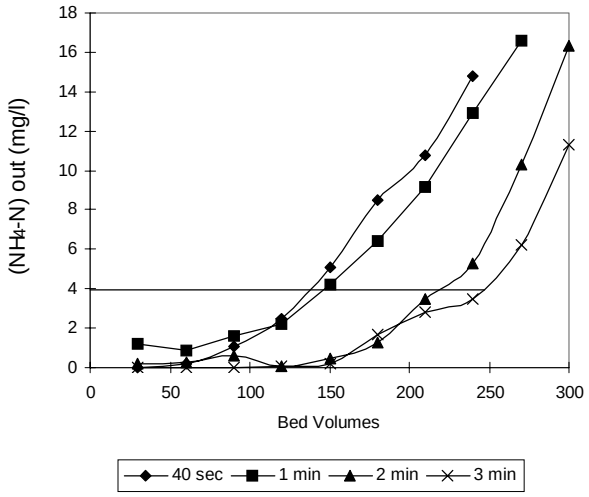

Figure 3
Breakthrough curves of virgin chabazite at different retention times

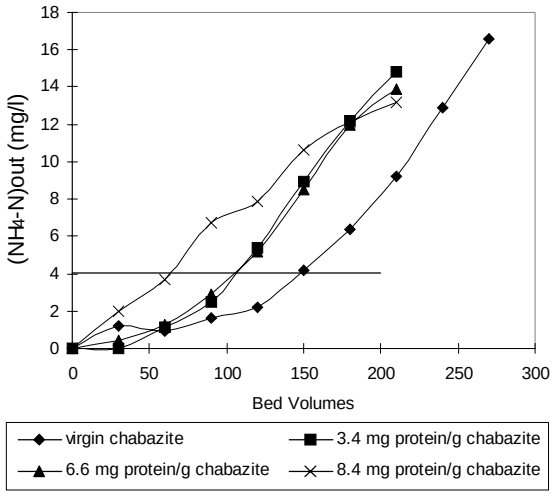

Figure 4
Breakthrough curve with retention time of 60 s

This biomass concentration was the highest concentration established during this research project. The ion-exchange kinetics of both virgin and biofilm-covered chabazites are shown in Fig. 2. The virgin chabazite showed a higher ion-exchange rate and reached approximately 93% (2.6 meq/g) of the equilibrium value after 120 min, while for the same period of time the biofilm-covered chabazite reached only about 70% (2.0 meq/g) of the equilibrium value. No significant difference between the total equilibrium capacity of the virgin chabazite and the biofilm-covered chabazite was found (both reached about 2.6 meq/g after 600 min).

Continuous experiments

Several adsorption experiments were conducted to compare between breakthrough curves of virgin chabazite and chabazite covered with various concentrations of biofilm.

Results for the virgin chabazite are given in Fig. 3. The breakthrough experiments were carried out at different retention times: 40, 60, 120, and 180 s.

An ammonium concentration of 4.0 mg/ℓ in the effluent was adopted in all experiments as the breakthrough point.

As can be seen from Fig. 3, the minimal retention time for efficient ion exchange is approximately 2.0 min. Shorter retention times resulted in early breakthrough while longer retention times were not significantly advantageous.

Results of ammonium breakthrough experiments for biofilm covered chabazite at different retention times (60 s and 120 s) and different biofilm concentrations are given in Figs. 4 and 5.

The results of 60 s retention time experiments showed that breakthrough occurred after 150 BV in the virgin chabazite, 100 BV in the chabazite covered with 3.4 and 6.6 mg protein/g chabazite and 60 BV in the chabazite covered with 8.4 mg protein/g chabazite. The results of the 120 s retention time experiments showed that breakthrough occurred after 220 BV in the virgin chabazite, 180 BV in the case of chabazite covered with 6.6 mg protein/g chabazite and 150 BV in the case of chabazite covered with 8.4 mg protein/g chabazite.

Since the batch experiments to determine ion-exchange total capacity indicated that the presence of the biofilm had not changed the total capacity, it was assumed that the deterioration of the ion-exchange rate was of a kinetic origin. However, in order to

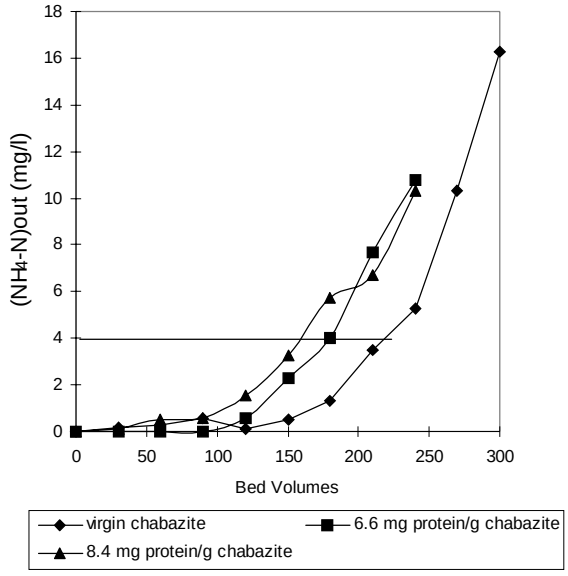

Figure 5
Breakthrough curve with retention time of 120 s

eliminate the possibility that the deterioration was due to loss in capacity, another set of batch experiments to compare between the total capacity of the virgin chabazite and the biofilm-covered chabazite, was carried out. The results (Table 2) showed no significant difference between covered and exposed chabazite.

Results of the first stage of experiments indicated a deterioration in ion-exchange rate in the biofilm-covered chabazite. This rate reduction was more significant for short retention times and high biomass concentrations than for longer retention times and/or low biomass concentrations. Another conclusion is that the chabazite does not lose its adsorption capacity as a result of the biofilm coverage. If the chabazite is left for enough time to reach equilibrium, full capacity is eventually reached.

The ion-exchange rate-controlling step: With and without biofilm

Rate control by either pore or film diffusion can be distinguished either experimentally or mathematically.

Mathematically

The rate-controlling step can be predicted by the following equation (Helfferich, 1962):

(1) $\frac{X\bar{D}\delta}{CDr_0}\left(5+2\alpha_B^A\right)<<1$ pore diffusion control

(2) $\frac{X\bar{D}\delta}{CDr_0}\left(5+2\alpha_B^A\right)>>1$ film diffusion control

where:

X = concentration of fixed ionic groups (1.4 eq/ℓ chabazite)
C = concentration of solution (approximately 18 meq/ℓ typical concentration of Israeli secondary effluent)
D = pore diffusion coefficient (10^{-8} cm^2/s)
$\bar{D}$ = film diffusion coefficient (10^{-5} cm^2/s)
r_0 = mean bead radius (0.15 cm)
δ = film thickness (10^{-3} cm)
α_B^A = separation factor (3.4 = separation factor NH_4^+ - Na^+)

Substituting the numerical values in the equation yields the following:

(3) $(1.4_{eq/\ell} \times 10^{-8}{}_{cm\text{^}2/sec} \times 10^{-3}{}_{cm})/(18 \times 10^{-3}{}_{eq/\ell}\ 10^{-5}{}_{cm\text{^}2/sec} \times 0.15_{cm})$ $\times (5+2*3.4) = 6.2 \times 10^{-2}<<1$

This result indicates that in an ion-exchange process using chabazite and typical simulative Israeli secondary effluent, pore diffusion is the rate-controlling step.

Experimental interruption tests

Results for the breakthrough curves of the virgin chabazite with and without 'interruptions' are shown in Fig. 6. The results show that the 'interruptions' (one after 3.5 h and another after 5.5 h) in the virgin chabazite were followed by an immediate higher adsorption rate (lower NH_4^+-N concentrations in the outflow). The non-interrupted chabazite breakthrough curve did not show the same phenomenon. These results indicate that 'pore diffusion' is the rate-limiting step for virgin chabazite.

Interruption test was also applied to the biofilm-covered chabazite (biofilm concentration: 8.4 mg protein/g chabazite) and the results are shown in Fig. 7. No evidence of change in the breakthrough curve as a result of the 'interruptions' (after 2.5 and 4 h) in the adsorption was observed, and the breakthrough curves with and without 'interruptions' were practically identical, indicating that 'film diffusion' is the rate-controlling step for chabazite-covered biofilm.

TABLE 2
ION-EXCHANGE CAPACITY OF VIRGIN AND BIOFILM-COVERED CHABAZITE

Resin type	Chabazite capacity (meq/g chabazite)
Virgin chabazite	2.78
Chabazite with 3.4 mg protein/g chabazite	2.66
Chabazite with 8.3 mg protein/g chabazite	2.70

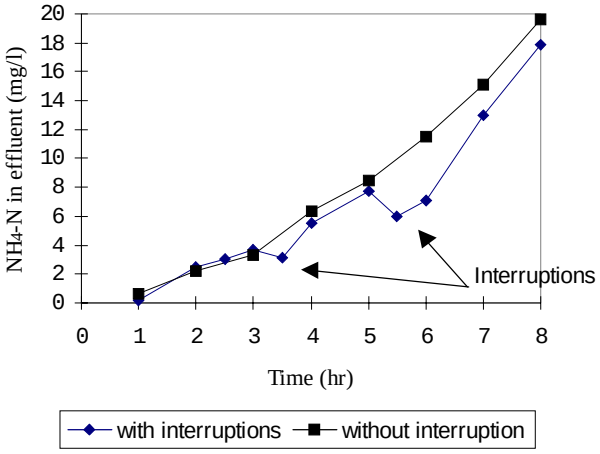

Figure 6
Interruption test for virgin chabazite

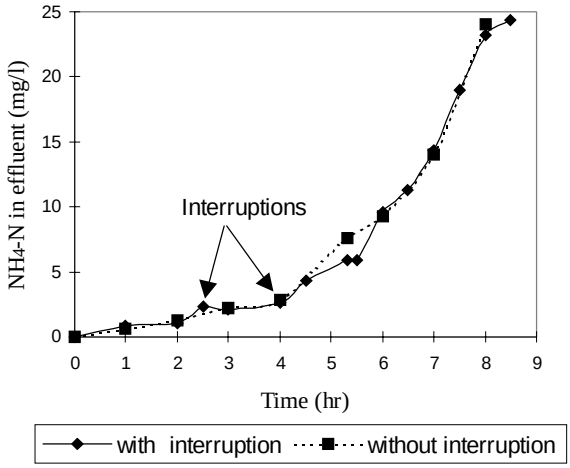

Figure 7
Interruption test for biofilm-covered chabazite

The results indicate that the ion-exchange rate-controlling step was shifted from pore diffusion in the virgin chabazite, to film diffusion in the biofilm-covered chabazite.

Surface barrier as a possible explanation to the shift in the rate-controlling mechanism

Diffusion in ion exchangers can sometimes be influenced by the presence of surface barriers which add resistance to ion transport. Such surface barriers can either cover the external area of the

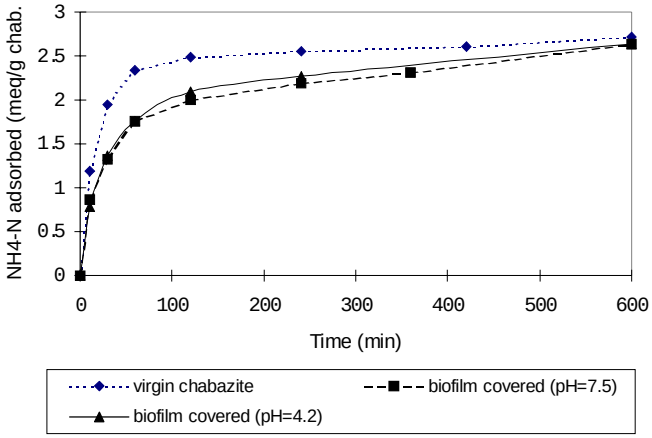

Figure 8
A comparison between biofilm-covered chabazite kinetics after conditioning in pH = 7.5 and pH = 4.2

particle completely, or cover it in a patchy manner, thus decreasing the area available for the free transportation of ions. In these cases, it is possible that the rate-limiting step would be changed from 'pore diffusion' to 'film diffusion'. These surface barriers could either be a part of the biofilm or a separate layer. The formation of such a layer which acts as a surface barrier can result from deposition of organic molecules on the ion-exchanger particles, or from precipitation of inorganic salts (iron oxides, calcium carbonate, magnesium hydroxide and other precipitates). The formation of inorganic precipitate is less probable at the low pH conditions prevalent during the bioregeneration phase, due to the release of H^+ ions during nitrification. In order to prove this point, batch experiments at low pH were conducted. A biofilm-covered chabazite was immersed in a pH = 4.2 solution for 8 d and subsequently a batch kinetic test was conducted. At conditions of such a low pH, with sufficient time to reach equilibrium, mineral precipitates, if they exist, should dissolve.

Figure 8 shows the results of this test. No significant change in ammonium adsorption rate due to lower pH conditions and mineral dissolution (pH = 4.2 vs. pH = 7.5) was observed. These results indicate that the deterioration in the ion-exchange rate was not caused by mineral deposition.

Organic fouling due to oil, grease, fats and proteins as well as adsorption of large organic ions originating from decaying biomass is a well-known phenomenon. However, this is more typical in the case of strong base anion exchangers and much less in the case of cation exchangers (Pelosi and McCarthy, 1982). Since the observed decrease in ion-exchange kinetics occurred even when the reactor was fed with simulated effluent (tap water + ions), organic fouling caused by oil or grease can be excluded. Fouling due to organic material originating from biological cellular material, i.e. polysaccharides or glycoproteins, which are the major constituents of the biofilm matrix, is more likely to occur in our case. Indeed, a gradual decrease in diffusion coefficient with biofilm depth together with a corresponding increase in biofilm density was reported by several authors (Bishop et al., 1995; Zhang and Bishop, 1994). However, this reported decrease is only up to one order of magnitude, therefore, not sufficient to explain the shift from pore to film diffusion (difference of about 3 orders of magnitude). This contradiction might be explained by the methods used in these studies which were on a micron scale, thus unable to discriminate very thin layers adjacent to the carrier, which usually are of no interest. Yet, in the unique case where the carrier actively participates in the process (ion exchanger), this thin layer could be the reason for the deterioration in the exchange kinetics observed. Therefore, it can be hypothesised that the part of the biofilm adjacent to the zeolite (perhaps several nanometres thick) has a much higher density than the rest of the biofilm, with the accompanying very low diffusion coefficient that could become the rate-limiting factor for the ion-exchange process, and the cause for the reduction in the ion-exchange rate in the biofilm-covered chabazite.

Summary and conclusions

A new concept for ammonia removal from secondary effluent using ion exchange (chabazite) and bioregeneration was developed. This paper reports the effects of biofilm coverage on zeolites on ion-exchange capacity and kinetics. The major conclusions are:

- Ion-exchange breakthrough curves of biofilm-covered chabazite showed deterioration in comparison to virgin chabazite (a maximal drop of approximately 30% in the time to breakthrough with retention time of 120 s). This phenomenon was observed when the reactor was fed either with simulated effluents or with actual effluents. The deterioration was greater with higher biofilm concentrations. The total ion-exchange capacity of the chabazite was not affected by the biofilm coverage. The results indicate that the deterioration in the breakthrough curves is due to a change in the ion-exchange kinetics.
- Batch kinetic experiments showed reduction in the ion-exchange rate in biofilm-covered chabazite as compared to virgin chabazite (a drop of 25% in the amount adsorbed after 120 min).
- Results from 'Interruption Test' experiments conducted to identify the ion-exchange rate-controlling mechanisms indicate that the rate-controlling step shifted from pore diffusion, in the virgin chabazite, to film diffusion in the biofilm-covered chabazite.
- The batch experiment at low pH indicated that chemical precipitation was not the cause for the ion-exchange rate reduction.

Based on the reduction in the ion-exchange rate and the change in the rate-controlling step from pore diffusion in the virgin chabazite to film diffusion in the biofilm-covered chabazite, a possible conjecture is that the biofilm is the major factor responsible for the deterioration in the ion-exchange rate. However, reported values for the diffusion coefficient of NH_4^+ inside biofilms are of the same order of magnitude as diffusion coefficients of NH_4^+ in water and 3 to 4 orders of magnitude greater than typical pore diffusion coefficient in zeolites. Based on those, the biofilm covering the chabazite is not supposed to affect the ion-exchange rate.

This apparent contradiction can be resolved when considering the reported values for biofilm diffusion coefficients as averaged values which do not represent the true conditions in the immediate vicinity of the carrier. Several authors report a decrease in the diffusion coefficient accompanied with an increase in the biofilm density in the inner layers of the biofilm. Therefore, it can be hypothesised that the part of the biofilm adjacent to the zeolite (perhaps several nanometres thick) has a much higher density than the rest of the biofilm, thus resulting in a much lower observed diffusion coefficient that could become the limiting factor for the ion-exchange process and the cause for the reduction in the ion-exchange rate in the biofilm-covered chabazite.

References

AMES L (1965) Self diffusion of some cations in open zeolites. *Am. Mineral*. **50** 465.

ARVIN E and KRISTENSEN G H (1982) Effect of denitrification on the pH in biofilms. *Water Sci. Technol.* **14** 833-848.

BISHOP DF, O'FARRELL TP, STAMBERG JB (1972) Physical-chemical treatment of municipal wastewater. *J. Water Pollut. Control Fed.* **44** 361-371.

BISHOP LB, ZHANG TC, FU Y (1995) Effects of biofilm structure, microbial distributions and mass transport on biodegradation processes. *Water Sci. Technol.* **31** (1) 143-152.

BRADFORD M M (1976) A rapid and sensitive method for the quantification of microgram quantities of protein utilizing the principle of protein-dye binding. *Anal. Biochem*. **72** 248-254.

CHARACKLIS WG (1990) Chapter 7. In: Characklis WG and Marshall KC (eds.) *Biofilms.* Publisher: John Willey & Sons, Inc.

CHERRY JM (1987) Contact Nitrification: Application of Zeolites to Contact Stabilization Activated Sludge. D.Sc. Thesis, Technion - Israeli Institute for Technology.

DYER A (1988) *Zeolite Molecular Sieves.* John Wiley and Sons, Inc.

FLYNN BP, ROBERTACCIO FL, BARRY LT (1976) Truth or consequences: Biological fouling and other considerations in the powdered activated carbon - activated sludge system. *Proc. 31st Purdue Ind. Waste Conf.* 855 pp.

GREEN M, MELS A, LAHAV O and TARRE S (1996) Biological ion exchange process for ammonium removal from secondary effluent. *Water Sci. Technol.* **34** 449-458.

HELFFERICH F (1962) *Ion Exchange.* McGraw - Hill Book Company, Inc.

KRESSMAN TRE and KITCHENER JA (1949) Cation exchange with a synthetic phenolsulphonate resin. Chromatographic Analysis. *Discussion of the Faraday Society* **7** 90-104.

LAHAV O and GREEN M (1998) Ammonium removal using ion exchange and biological regeneration. *Water Res.* **32** (7) 2019-2028.

LOWRY JD and BURKHEAD CE (1980) The role of adsorption in biologically extended activated carbon columns. *J. Water Pollut. Control Fed.* **52** 389-398.

NAKHLA GF and SUIDAN MT (1995) Effect of anaerobic biological activity on the adsorptive capacity of granular activated carbon. *Water Environ. Res*. **67** 1020-1026.

NEVEU A, GASPARD M, BLANCHARD G and MARTIN G (1985) Intracrystalline self-diffusion of ions in clinoptilolite ammonia and sodium cations studies. *Water Res.* **19** 611-618.

PELOSI P and McCARTHY J (1982) Preventing fouling of ion exchange resins - 1. *Chem. Eng.* **8** 75 - 79.

SEMMENS MJ and PORTER PS (1979) Ammonium removal by ion exchange: Using biologically restored regenerant. *J. WPCF* **51** (12) 2928 - 2940.

SHULTZ JR and KEINATH TM (1984) Powdered activated carbon treatment process mechanisms. *J. Water Pollut. Control Fed.* **56** 143-151.

STANDARD METHODS (1992) *Standard Methods for the Examination of Water and Wastewater* (18th edn.). APHA - AWWA - WPCF, USA.

WILIAMSON KF and McCARTY PL (1976) A model of substrate utilization by bacterial films. *J. Water Pollut. Contr. Fed.* **48** 9-24.

ZHANG T and BISHOP P (1994) Structure, activity and composition of biofilms. *Water Sci. Technol.* **29** (7) 335-344.