Practical Paper

Ion exchange with clinoptilolite to control ammonium in drinking water

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ABSTRACT

Ammonium is one of the objectionable constituents in drinking water and water supply reservoirs. Removal of ammonium from water supply resources is sometimes necessary for acceptable drinking water quality. Ion exchange with the ammonium selective natural zeolite clinoptilolite, is proposed as one possible option for this purpose. The capacity and success of clinoptilolite for ammonium removal under those conditions have been investigated. The results from both batch isotherm experiments and continuous column runs have shown that the process is indeed effective. However, the competing ions mostly in the form of hardness impact with the potential capacity significantly. Depending upon conditions prevailing, over 50% of the capacity may be used by the competing ions, reducing the capacity intended for the targeted ammonium ions, however the limits for ammonium for drinking water could be achieved under all circumstances without problems.

Key words | ammonium removal, clinoptilolite, drinking water, ion exchange, low ammonium concentration, natural zeolite

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INTRODUCTION

Although nitrogen is one of the essential elements of life, its presence in excess may lead to significant problems in natural water bodies and drinking water supply reservoirs including eutrophication. If nitrogen exists as ammonia, additional depletion of oxygen and fish toxicity may also be expected. Nitrogen in the nitrate form is undesirable in drinking water due to methemoglobinemia, the blue baby syndrome. Ammonia in drinking water is also objectionable and limits have been issued by the European Union as well as the Turkish drinking water regulations as 0.05 mg NH_4^+/l as the guide level and 0.5 mg NH_4^+/l as the maximum permissible concentration (Council Directive 1980; TSE 266 1997).

The European Union Directive for the abstraction of water for public consumption from water resources lists Classes 1, 2 and 3 as acceptable classes for drinking water supply and states the guide and mandatory limits as 0.05 and 0.5 mg NH_4^+/l, 1 and 1.5 mg NH_4^+/l and 2 and 4 mg NH_4^+/l for first, second and third class water, respectively (Council Directive 1975). The inland surface water classification of the Turkish Water Pollution Control Regulation indicates an ammonium nitrogen concentration of 0.2 mg NH_4^+-N/l and 1 mg NH_4^+-N/l for first and second class water, respectively, which are advised as the relevant classes for water supply (TWPCR 2004). However, values from drinking water supply reservoirs as high as 10–15 mg NH_4^+-N/l had been reported in the literature (Hlavay et al. 1983; Turan et al. 1999).

One of the successful methods of ammonium removal from water and wastewater of different character is ion exchange with the ammonium selective natural zeolite clinoptilolite and the order of selectivity in comparable

concentrations is given by Koon & Kaufman (1975) as

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+}$$
$$> Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$$
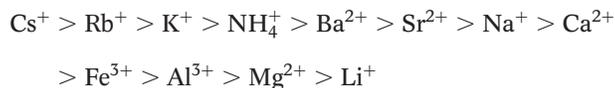
There has been a considerable amount of work devoted to the removal of ammonium from wastewater through the use of clinoptilolite to show that the process was successful under a wide spectrum of conditions (Ames 1967; Mercer et al. 1970; McLaren & Farquahar 1973; Semmens et al. 1977; Semmens & Porter 1979; Hlavay et al. 1982; Schoeman 1986; Beler Baykal et al. 1994; Oldenburg & Sekoulov 1995; Beler Baykal et al. 1996; Booker et al. 1996; Beler Baykal & Akca Guven 1997; Komarowski & Yu 1997; Beler Baykal 1998; Nguyen & Tanner 1998; Gisvold et al. 2000a, 2000b; Inglezakis et al. 2001; Rother & Cornel 2004; Beler Baykal et al. 2005; Inan & Beler Baykal 2005; Jorgensen & Weatherley 2006). A review of the process together with a summary of previous work has been published by Hedstrom (2001). Most of that work was directed towards relatively higher concentrations of ammonium, i.e. mostly within the range that may be expected in domestic wastewater. The literature on the system behavior and capacity regarding the removal of ammonium from water with low concentrations like those expected in drinking water resources or in actual drinking water is very limited (Gaspard et al. 1983; Hlavay et al. 1983; Reynolds & Williford 1988; Hodi et al. 1995; Turan et al. 1999).

As was indicated earlier, high concentrations of ammonium is objectionable in drinking water and concentrations exceeding 0.5 mg/l are not recommended for drinking purposes. To be able to maintain that level in water intended for human consumption, ammonium would have to be removed from water supplies which are supposed to have a relatively low concentration, normally 4 mg/l or less, as advised by the regulations mentioned before. On the other hand, ion exchange equilibrium dictates that the surface concentrations on the ion exchanger will be lower for lower solution concentrations, meaning that the surface capacity of the ion exchanger expressed as the quantity of ammonium held on the ion exchanger per mass of ion exchanger, will decrease as water with low concentrations of ammonium are dealt with. With water supplies as well as drinking water, the interference

through the competition of hardness ions is still to be kept in mind in predicting the capacity of the ion exchanger. A review of the order of selectivity reveals that provided that they exist in comparable concentrations ammonium will be preferred over calcium, which in turn will be preferred over magnesium. Literature regarding this competition is also extremely limited (Hlavay et al. 1983; Reynolds & Williford 1988).

This work aims to present the results from batch isotherm experiments in an effort to quantify the capacity of ion exchange under those circumstances, and to observe the behavior of the ion exchange system as ammonium is removed from water with low ammonium concentrations in continuous columns, in the presence of competing hardness ions. Ammonium removal from two different water samples in terms of hardness through ion exchange with clinoptilolite was investigated. Within this context, extensive data from batch isotherm experiments will be presented to quantify capacity and the breakthrough analysis will be presented to reflect system behavior in continuous flow columns.

METHOD

This work was undertaken primarily to investigate the success of ammonium removal from water with low concentration of ammonium *via* ion exchange with a Turkish clinoptilolite by running extensive isotherm work. The effect of hardness on ion exchange capacity as a source of competing ions was also investigated. Additionally, breakthrough behavior was observed at different contact times in fixed bed columns under continuous operation.

The clinoptilolite used in the experiments was from the Western Anatolian region of Turkey, namely Bigadic, with a typical composition of 80.19% SiO_2, 11.2% Al_2O_3, 3.46% CaO, 2.37% K_2O, 1.79% FeO, and less than 1% of MgO and Na_2O (Inan & Beler Baykal 2005). The particle size range used was 1–2 mm. After the clinoptilolite was brought to the desired particle size, it was washed with distilled water several times, then conditioned with 1 M NaCl to prepare the sodium form, which had been previously shown to be the most effective form of the zeolite for ammonium removal. A flowrate equivalent to one bed volume per

hour was used for conditioning in the continuous fixed bed column filled with original clinoptilolite for a duration of two days. In all experimental runs, virgin clinoptilolite in the sodium form was used.

Two different types of drinking water, enriched with ammonium chloride as necessary, were used: bottled spring water to represent soft water and tap water supplied by the municipality of Istanbul to represent water of intermediate hardness. Raw water samples were characterized for ammonium, total hardness, calcium, magnesium and pH and their characteristics are given in Table 1.

As can be concluded from Table 1, 85% of the total hardness in tap water comes from calcium. The corresponding percentage for soft water is 82%. With those results, and the fact that magnesium ions are preferred considerably less by clinoptilolite than calcium, calcium was taken as the significant ion which would compete with ammonium.

Ammonium measurements together with calcium, reported in a previous paper by Cinar & Beler Baykal (2005), were made routinely throughout the experimental work. Total hardness was also measured intermittently. Ammonium was determined *via* Orion ion meter and ammonium probe while the EDTA titrimetric method of *Standard Methods* (1998) was used for calcium and total hardness.

Both batch and continuous system runs were undertaken. In the first part, isotherm experiments were made in batch systems where the water samples with known concentrations were contacted with clinoptilolite at $20 \pm 2°C$ for 24 hours in a shaker to reach equilibrium. Sample sizes of 250 ml were used. Raw water samples shown on Table 1 were enriched with ammonium chloride to attain initial concentrations of $1-10$ mg NH_4^+/l before being shaken with clinoptilolite samples of $0.2-4.5$ grams. Samples from the liquid phase were analyzed for ammonium and the solid phase concentrations were calculated from the knowledge of the initial

and final liquid phase concentrations, the sample size and the amount of clinoptilolite used.

In the second part of the experiment, breakthrough behavior in fixed bed columns under continuous flow was investigated using tap water of intermediate hardness. The feed water was enriched with NH_4Cl to maintain an influent concentration of 5 ± 0.5 mg NH_4^+/l. Columns of 100 cm length and 2.6 cm diameter were operated in the upflow mode. Contact times used in the runs were 3.5, 5, 7 and 10 minutes. Effluent samples were taken regularly *via* autosampler and the samples were analyzed for ammonium. Details of this group of experiments are given in Table 2.

RESULTS AND DISCUSSION

The success of ammonium removal from water with relatively lower concentrations of ammonium in the presence of competing hardness ions was investigated in this piece of work. Within this context, first the capacity of clinoptilolite for removing ammonium was determined through extensive batch isotherm experiments under different conditions. Two different hardness levels were used. Thereafter, breakthrough behavior was investigated in continuous columns.

In the first part of the experiments isotherms for two different types of drinking water in terms of hardness were employed: bottled spring water, to represent soft water, and tap water supplied by Istanbul Municipality to represent intermediate hardness water. Isotherms were generated for the concentration range of $0-5$ mg/l from the measurement of liquid phase equilibrium ammonium concentrations and corresponding calculated solid phase concentrations at the

Table 1 | Raw water characteristics

	Total hardness (mg CaCO$_3$/l)	Ca^{2+} (mg CaCO$_3$/l)	Mg^{2+} (mg CaCO$_3$/l)	NH$_4^+$ (mg/l)	pH
Soft (spring water)	36.4	29.7	6.7	<0.05	7.03
Intermediate (tap water)	122.8	103.6	18.8	<0.05	7.50

Table 2 | Details of the breakthrough runs

Flowrate ml/min	Contact time minutes	Bed heigh cm	Mass of zeolite g
15	3.5	10	42.1
10	5	9.5	40.0
15	7	20	84.2
10	10	19	80.0

particle size range of 1–2 mm. Validity of the linear, Langmuir and Freundlich isotherm models were tested.

Figure 1 presents the isotherm for soft water. The results of the isotherm model tests have given regression coefficients as 0.9392, 0.8329 and 0.9319 for the linear, Langmuir and Freundlich models, respectively. As can be observed, the best fit was obtained for the linear model, which is also shown in the figure. This is in contrast with the ammonium isotherms for wastewater, which are best represented by monolayer isotherm models, i.e. Langmuir and Freundlich. The best isotherm equation to describe the lower concentration system observed was determined to be

$$q_e = 1.4077\,C_e + 0.5396$$

where C_e is the equilibrium liquid phase concentration in mg NH_4^+/l, and q_e is the corresponding surface concentration of ammonium in mg NH_4^+/g of clinoptilolite. Surface capacities in equilibrium with the guide level of 0.05 mg/l was calculated to be 0.61 mg NH_4^+/g of clinoptilolite and the corresponding surface concentration
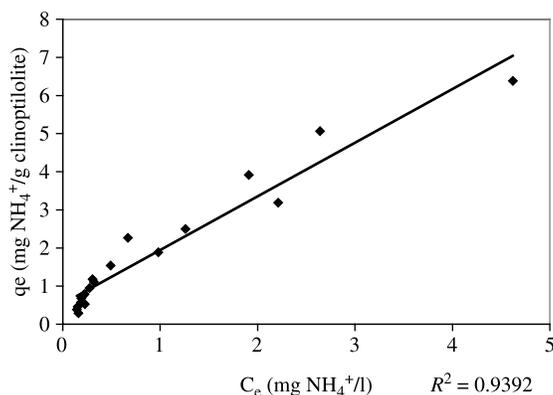
Figure 1 | The ion exchange isotherm and the linear model for soft water and clinoptilolite with 1–2 mm particle size.
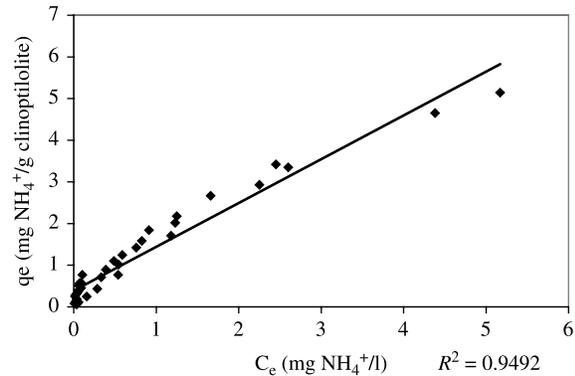
Figure 2 | The ion exchange isotherm and the linear model for intermediate hardness water and clinoptilolite with 1–2 mm particle size.

for the maximum admissible concentration of 0.5 mg/l was 1.24 mg NH_4^+/g of clinoptilolite.

A similar type of analysis was also performed with tap water which represented intermediate hardness to give the isotherm in Figure 2. This time the resulting regression coefficients were 0.9492, 0.4786 and 0.8645 for the linear, Langmuir and Freundlich models, respectively. Again, the best fit was obtained with the linear model, shown in the same figure, and the best isotherm equation was determined to be

$$q_e = 1.0522\,C_e + 0.3876$$

where once again C_e is the equilibrium liquid phase concentration in mg NH_4^+/l, and q_e is the corresponding surface concentration of ammonium in mg NH_4^+/g of clinoptilolite. Surface capacities in equilibrium with the recommended ammonium value of 0.05 mg/l was calculated as 0.44 mg NH_4^+/g of clinoptilolite and the corresponding surface concentration for the maximum allowable value of 0.5 mg/l was 0.91 mg NH_4^+/g of clinoptilolite.

A comparison of the surface capacities for ammonium clearly reveals that the level of hardness has a significant effect upon the outcome of the ion exchange process. Figure 3 presents a comparison of surface capacities of 1–2 mm clinoptilolite for ammonium. The "distilled water" isotherm represents the surface capacity of the 1–2 mm clinoptilolite for ammonium with a pure solution of ammonium chloride in distilled water, where no competing ions exist. The figure shows the effect of competing ions even more clearly. At a solution concentration of 5 mg NH_4^+/l, surface concentrations of about 14, 7, and 5 mg NH_4^+/g clinoptilolite could
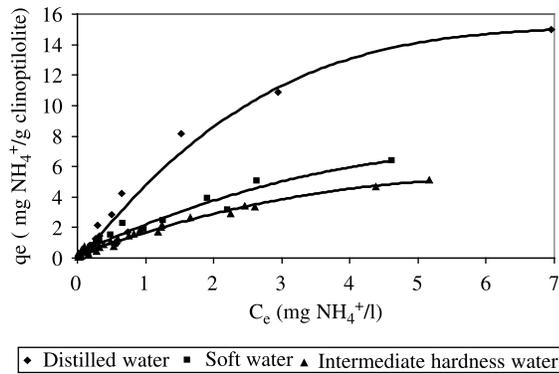
Figure 3 │ The effect of competing ions on ammonium removal capacity for 1–2 mm clinoptilolite.

Figure 4 │ Breakthrough curves for intermediate hardness water for $C_0 = 5$ mg/l.

be attained for ammonium removal from distilled water, soft water and intermediate hardness, respectively. A comparison of the isotherms and those capacities reveals that over 50% of the exchange capacity is actually used by the competing ions. The serious impact of the competition on the ammonium removal capacity is obvious. This would mean that the level of success of clinoptilolite, which can clearly be used for the removal of ammonium from water with low concentrations of ammonium, is closely related to the concentration of hardness ions. This outcome had been expected qualitatively since the concentrations of ammonium and competing ions were not compatible. Although at similar concentrations, clinoptilolite has a high selectivity towards ammonium, under the conditions employed, competing ions would have an advantage. This work has provided quantitative data to support this expectation.

In the second part of the experiments, breakthrough analysis was carried out to observe system behavior under continuous flow conditions between contact times of 3.5 and 10 minutes. Lower contact times were shown to be unsatisfactory in previous work with wastewater (Beler Baykal 1998). The results for intermediate hardness tap water with an influent concentration of 5 mg/l and a clinoptilolite particle size of 1–2 mm are presented in Figure 4. It may be observed that 90% ammonium removal to achieve drinking water quality of the maximum allowable limits could be maintained for 20, 35, 53 and 92 hours for contact times of 3.5, 5, 7, and 10 minutes, respectively, again indicating the success of the process. It is to be noted that these results are for intermediate hardness water and a more
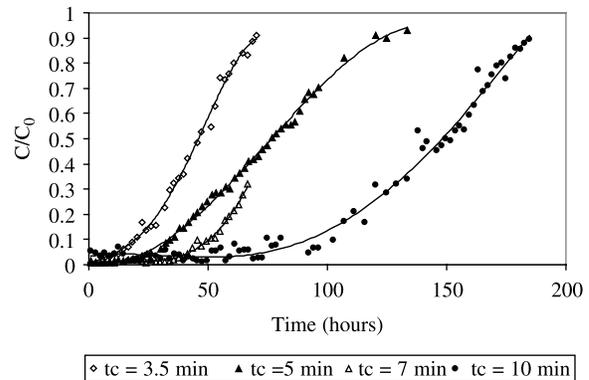
efficient removal with longer operating times before regeneration should be expected for influents of lower hardness levels.

CONCLUSIONS

The laboratory results evaluating the use of ion exchange with clinoptilolite for the removal of ammonium from water for drinking water purposes has indicated that the process offers a successful alternative in terms of capacity and treatability. Within the range of $0–5$ mg NH_4^+/l of solution concentration, surface concentrations as high as 14, 7, and 5 mg NH_4^+/g clinoptilolite could be attained for ammonium removal from distilled water, soft water and water of intermediate hardness, respectively. A very important point to consider was the effect of competing ions mostly due to hardness, which could occupy over 50% of the ion exchange capacity. However, the desired ammonium removal could still be attained under all circumstances evaluated. This indicates that for an effective removal practice to attain targeted ammonium levels, correct amounts of the zeolite should be used taking into account provisions for competing ions.

The breakthrough analysis run in continuous columns has revealed that high removal efficiencies could be attained and the efficiencies could be increased by increasing the contact time as expected, to maintain 90% efficiency for up to four days without necessitating the renewal of the zeolite under the conditions investigated.

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