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Short Communication

Zeolites in Marine Nitrogen Transformations

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ABSTRACT

The decomposition of unconsumed food is one of the ammonium sources in aquaculture. In an earlier work we studied the action of zeolites on ammonium elimination and we found an effective reduction of this cation but if zeolite is present in small doses, it seems that it potentiates ammonium formation, and produces possibly a catalytic action to which zeolitic products are disposed, or stimulates the microbial activity.

In the present work we studied the possible influence of a zeolite on the transformation of ammonium to nitrite in conditions of normal oxygenation and under artificial oxygenation in sea water. We also report on the effect of zeolite on NH_4^+ *appearance produced by fish food decomposition.*

INTRODUCTION

When the concentration of ammonium exceeds a certain limit, it becomes toxic to fish life, so that apart from its nutritive action in phytoplankton growth, it is advisable to eliminate it in aquaculture plants until suitable levels are obtained (Mumpton, 1977). In order to achieve this elimination, zeolites are used in fresh water aquaculture systems (Leonard, 1980) although their efficiency is enormously reduced in sea water (López-Ruiz & Fernández del Barrio, 1987).

Moreover, one of the sources of ammonium in aquaculture is the decomposition of unconsumed food, which is why in earlier work we studied the action of zeolites on the elimination of ammonium produced in this process (López-Ruiz & Pérez-Sánchez, 1990). We found that at certain concentrations of zeolite, an effective reduction of ammonium occurs, but if the zeolite is present in small doses, it seems that it then potentiates ammonium formation, with this cation appearing in greater quantity than usual. It would seem, therefore, that ammonium forms part of the biological nitrogen cycle, albeit at the very start, and the presence of zeolite has possibly a catalytic action to which zeolites are disposed, or stimulates microbial activity. To investigate this effect we carried out the corresponding study (Chaves & López Ruiz, 1990), it being well known that microbial action leads to nitrification (the successive transformation of ammonium to nitrites and nitrates) in sea water (Ruá, 1990).

In the present work we studied the possible influence of a zeolite on the transformation of ammonium to nitrite in conditions of normal oxygenation and under artificial oxygenation in sea water. We also report on the effect of zeolites on the appearance of NH_4^+ produced by the decomposition of fish food.

MATERIALS AND METHODS

The experiments were carried out in triplicate, using beakers containing 2 litres of sea water (natural or artificial), with or without artificial aeration. We took samples for analysis periodically and sample volume was replaced with sea water. Any evaporation loss was replaced with distilled water.

We used natural sea water of 35% salinity, filtering through 0·45-μ Millipore (A series). In the second series of tests (B series), a solution of 3·5% by weight NaCl in distilled water was used in order to obtain a solution with an ionic strength similar to that of sea water.

Where the water was aerated artificially, the air was gently introduced through a glass tube at the bottom of the beaker.

The zeolites used were: (a) 13X Linde (commercial product) in extruded pellets approximately 1 mm in diameter and 2–3 mm long; (b) F Linde (commercial product), as a powder.

Fish food containing 38% protein was added to the water at 1 g litre^{-1}.

The average water temperature was 25°C.

The amount of ammonium present was determined by the indophenol spectrophotometric method. The presence of nitrites was determined, again using a spectrophotometer, by the coloration produced by sulfanilamide and *N*(1-naphthyl) ethylenediamine (Strickland & Parson, 1997).

EXPERIMENTAL RESULTS AND DISCUSSION

A Series

Firstly, a series of four experiments, using sea water, were carried out in order to test concentrations of NH_4^+ and NO_2^- at periodic intervals over the 135 days study. $NH_4^+(NH_4Cl)$ was initially added to this water in order to obtain the concentration mentioned later.

The study was carried out in order to learn the possible influence that forced aeration and the presence of zeolite, could have on the variation of ammonium concentration. For this purpose the following tests were devised: (a) no aeration, no zeolite; (b) aerated, no zeolite; (c) no aeration, zeolite present; (d) aerated, zeolite present.

Table 1 shows the results obtained, that is the concentrations of the aforementioned nitrogen forms (NH_4^+ and NO_2^-) throughout the 135 days' study. All concentrations have been referred to the same initial quantity of NH_4^+ (9·00 ppm). Figure 1 indicates the change in ammonium concentration.

In the light of these results we can deduce that artificial aeration by constant introduction of bubbles through the ammonia solution, noticeably reduces the levels of this cation: after 50 days there is a difference of approximately 2·5 ppm N(NH_4^+) with respect to the non-aerated

TABLE 1

Quantities of Nitrogen (mg N litre^{-1}) in NH_4^+ and NO_2^- over the 135 Days of Tests

No.	*Days*	$NH_4^{(a)}$	NO_2	$NH_4^{(b)}$	NO_2	$NH_4^{(c)}$	NO_2	$NH_4^{(d)}$	NO_2
1	0	9·00	0·15	9·00	0·15	9·00	0·17	9·00	0·16
2	0·2	8·80	0·15	8·50	0·16	—	—	8·24	0·17
3	1	6·51	0·13	7·05	0·14	7·14	0·16	6·78	0·14
4	3	8·14	0·14	7·79	0·13	8·52	0·16	7·90	0·14
5	7	6·58	0·11	5·68	0·14	6·52	0·16	5·66	0·14
6	23	6·76	0·10	4·38	0·15	7·76	0·17	5·19	0·24
7	38	6·03	0·10	2·73	0·16	4·23	0·12	3·02	0·26
8	47	1·79	—	0·94	—	0·92	—	0·56	—
9	66	3·67	0·09	1·20	0·13	2·20	0·01	0·67	0·09
10	84	3·71	0·09	0·78	0·12	2·04	0·01	0·47	0·07
11	100	3·04	0·09	0·69	0·13	0·62	0·01	0·36	0·02
12	120	—	0·08	—	0·10	0·32	0·01	0·32	0·01
13	135	1·78	0·08	0·46	0·10	0·46	0·01	0·43	0·02

samples, and 2·1 ppm after 100 days. After 135 days the difference is only 1·3 ppm.

The presence of 13X zeolite at a concentration of 1 g litre^{-1} also stimulates reduction of ammonium although only slightly. Thus, without bubbling, the zeolite is responsible for a drop in concentration of 1·5 ppm N(NH_4^+) after 50 days, 1·8 ppm after 100 days, and 1·3 ppm after

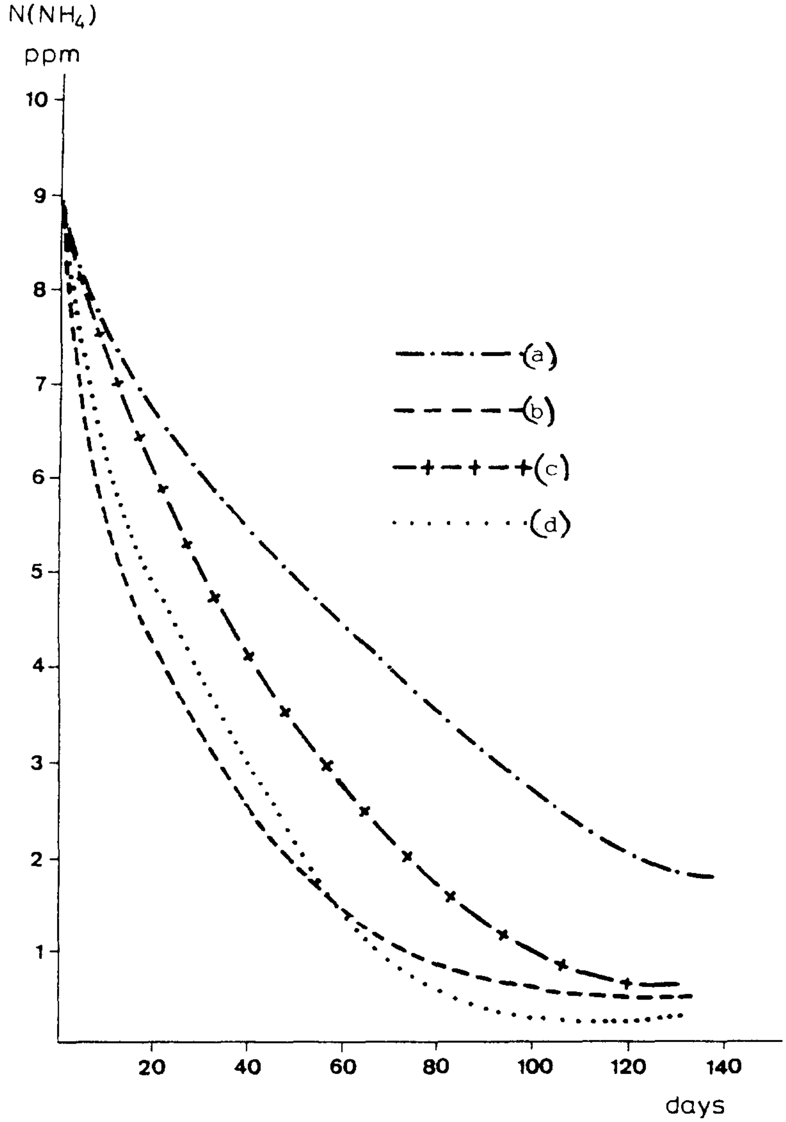

Fig. 1. Changes in NH_4^+ concentrations over the 135 days period, under conditions (a), (b), (c) and (d).

135 days. When air is bubbled through, the difference made by the zeolite is slight and initially of an opposite nature, 0·3 ppm higher with 13X after 50 days, 0·5 ppm lower after 100 days and almost the same difference after 135 days. That is to say that the decrease in ammonium concentration depends in the first place on forced aeration and secondly on the presence of zeolite.

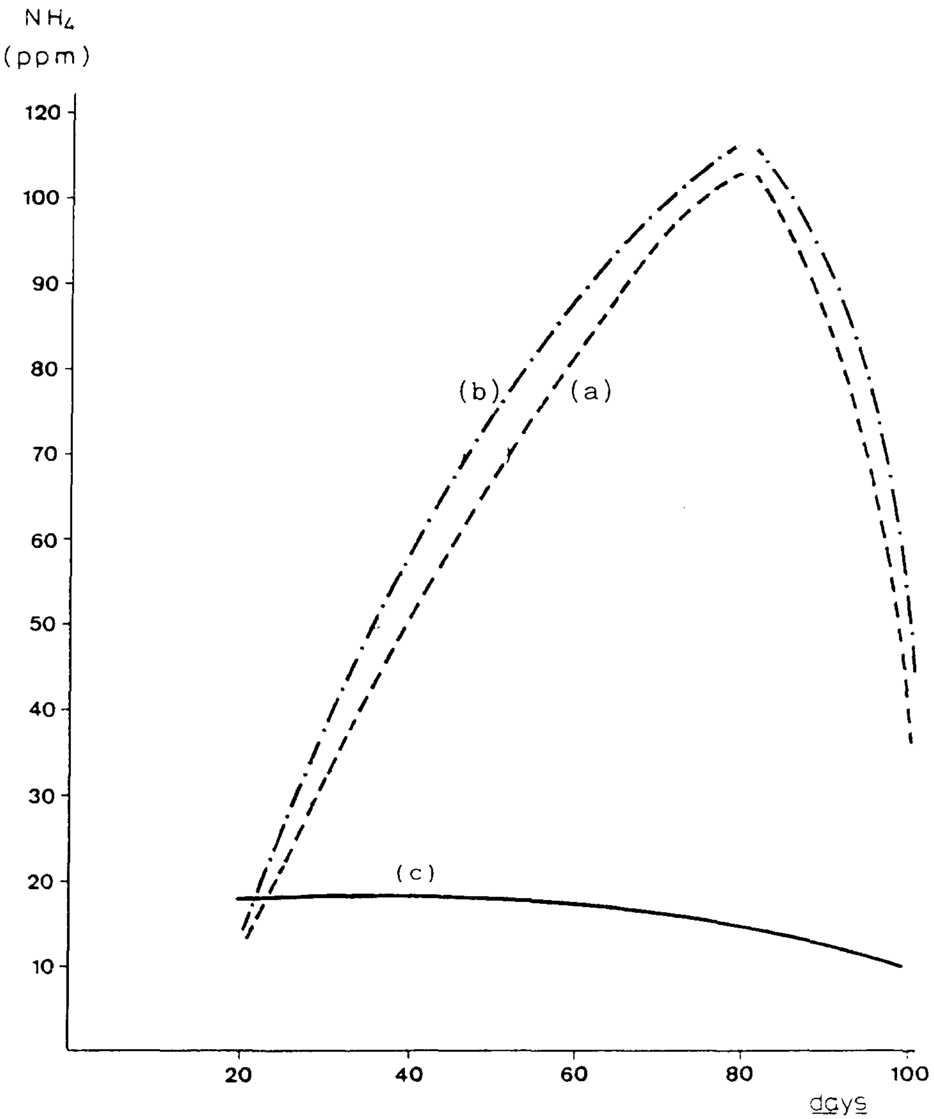

Fig. 2. Presence of NH_4^+ in the decomposition of fish food: (a) without zeolite; (b) with 0·5 g F Linde litre^{-1}; (c) with 25 g F Linde litre^{-1}.

It must be emphasised that in each of these processes the concentration of nitrites undergoes little variation, in comparison with ammonium variation. Nevertheless, it can be pointed out that without 13X the concentration of NO_2^- changes from 0·15 (at the start) to 0·10 ppm $N(NO_2^-)$, whilst with zeolite, the variation is from 0·17 (at the start) to 0·01 ppm, in both cases after 135 days.

B Series

In the context of zeolite action on ammonia processes here, like the other series of tests, we have found that F Linde zeolite, when present in small doses, had a positive action on the amount of NH_4^+ produced in the microbial decomposition of unconsumed food in aquaculture systems (Fig. 2). It can be seen that the presence of F Linde at 50% of the weight of suspended food (0·5 g $litre^{-1}$) in 3·5% NaCl solution increases the concentration of ammonium as compared to the samples where F Linde is absent, shown by lines (b) and (a) respectively in Fig. 2. On the other hand when F Linde zeolite is present at a level of 25 g $litre^{-1}$ (line (c), Fig. 2), the concentration of ammonium is much less, so confirming that zeolite products have an influence on the production of ammonium and on the transformation of nitrogen forms in general.

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