Treatment, by zeolitic products, for the elimination of ammonium contained in water of different salinities

P. M. Rodríguez Fernández, J. M. López Alcalá & J. L. López Ruiz
Centro Superior Estudios Marinos. Dpto.C. Navales
University of Cádiz, Spain.

Abstract

The ammonium elimination in continental waters is a problem solved by the action of zeolites, through cation interexchange. This is used, for example in factories in which the water reuse is a necessary process, or to avoid the increase of contamination due to wastes. In saline waters or in seawaters, the problem increases due to the saline cations inhibiting the interchange. So, it is necessary to improve the capacity of zeolites by the preparation of new varieties, named products of zeolitic nature (PZNs) with better yields, which have been obtained with this aim. Good results have been reached. By preparation of new PZNs, elimination of 20% of initial ammonium are reached. These are the best results referenced in the bibliography up to date. The results of ammonium elimination by PZNs, in seawater or in saline waters of different salinities, is studied in this paper.

1 Introduction

Ammonium is a contaminant of waters, included piscicultural ones, and its elimination (López Ruiz, 1988), is an important problem in waste waters, in order to reuse the water or to reduce the contamination. One method used with this aim employs zeolites and products of zeolitic nature (PZNs) (sodic aluminosilicates) by the utilization of the capacity for ammonium elimination of these products through cationic exchange. This is a well known technique utilized in contaminated continental waters, such as domestic or aquacultural residues (Mumptom, 1977). In later times the possibility of ammonium elimination has been admitted by different mechanisms rather than cation interexchange: perhaps byammonic complex with heavy metals existing in the zeolitic structure.

The problem of ammonium elimination by zeolites and PZNs, to re-use water and reduce ecological problems, appears when ammonium is present in sea or saline waters, due to the major existence of different cations (sodium, calcium, magnesium etc), in contrast to the ammonium concentration with which in general exists in waters (10 ppm). In these cases, the elimination capacities of PZNs is reduced a lot and it is necessary to probe new products containing larger capacity for the cited elimination.

To solve this problem our Group is studying several products and preparation methods of different zeolitic varieties (López Alcalá *et al,* 1998; Rodríguez Fuentes *et al*, 1998; López Alcalá and López Ruiz, 2001).

These products are natural zeolites and also, some products of zeolitic nature (PZNs) obtained in our Laboratory from the alkaline treatment of various starting materials such as bentonite, mordenite, ceramic wastes, steriles from carbon mines, etc (Ferreiro Almeda *et al,* 1998).

In this work we show some results of the assays for the retention of ammonium contained in waters of different salinities, by the action of specific PZNs which carried out more efficient ammonium elimination.

2 Materials and methods

The waters with variable salinities that have been used, are: distilled water (DI), domestic water (DO) with 23 French degree, diluted seawater with 1,75% of salinity (1,75%), and natural seawater with 3,5% of salinity (3,5%).

Zeolites are aluminosilicates which contain characteristic properties which allow applications in very different fields includying water depuration, specially for ammonium elimination, and cation exchange (Table I).

Several factors participate in synthesis which lead to optimum zeolitic product for ionic exchange. Good yields are achieved by use of special methods of optimisation, such as REVOP (Random Evolutionary Optimisation). The factors we studied in this method were: Molar rates of Al_2O_3 with SiO_2, Na_2O and H_2O, time of initial agitation, reaction time and temperature.

Table I: Cation exchange capacity (CEC) (meq/g) of some natural zeolites.

Zeolite	Molar rate Si/Al	CEC
Clinoptilolite	4.5	2.6
Mordenite	5	2.6
Erionite	3	3.8
Chabazite	2	5
Y	2	5
X	1.2	6.5
A	1	7

Table II indicates brief description of products utilized in the investigation related in this paper. Two types of synthesis are utilized. Type –06 is carried out with closed reactor, 72 hours and 160°C. Type –56 consists of open reactor, with agitation, 8 hours and 95°C (Ferreiro Almeda *et al,* 1998).

Table II: Zeolitic products, base materials and methods of preparation.

Name of products	Base materials	Preparation method
NZ	Cuban zeolita	Natural mineral
clinoptilolite	natural zeolite	- - -
zeolite 4/20	natural zeolite	- - -
Zecer-56.AM	ceramic wastes	Type 56 in seawater
Zecer-56	ceramic wastes	Type 56
Zeben-06	bentonite	Type 06
Zestec-06	carbon sterile	Type 06
Zemor-06	zeolite 4/20	Type 06
Mg.NZ	Cuban zeolite NZ	Exchanged with Mg^{2+}
Cu.NZ	Cuban zeolite NZ	Exchanged with Cu^{2+}
ZZ	Cuban zeolite NZ	Exchanged with Zn^{2+}
MZ	Cuban zeolite NZ	Exchanged with Mg^{2+}
H.NZ-450	Cuban zeolite NZ	Decationized

XRD of several products have been obtained. These XRD demonstrate the differences between starting materials and products obtained after treatment. Besides the ammonium eliminations with PZNs are better than with corresponding starting materials before treatment.

To know the elimination capacity of each PZNs, 1 g of them is agitated with 100 ml of solution of 10 mg NH_4^+/l in dissolvent with different salinities for 2 hours, at 25°C. The solutes have been before mentioned: DI, DO, 1,75% and 3,5%. The indophenol spectrophotometric method has been used to measure the ammonium concentration (Strickland and Parsons).

3 Experimental results and discussion

In Table III we show some results of eliminations obtained by several PZNs in sea and distilled waters, at 25°C.

Good eliminations have been obtained in some cases; the best, with Zecer-56 and PZ.Mg, with elimination up to 20% of initial content, in seawater. This is the best result registered up to date in the bibliography.

Table III: Residual concentrations (C, $mg.^{-1}$) and ammonium retentions ($R.10^{-3}$ $meq.g^{-1}$) by zeolitic products, in solutions containing 10 mg $NH_4^+.l^{-1}$ initially, indicating the elimination percentage (%).

	Distilled water			Seawater		
Products	C	R	%	C	R	%
Zecer-56.AM	-	-	-	8.0	11.1	20
Mg.NZ	1.3	48.0	87	8.2	10.0	18
Cu.NZ	2.4	42.0	76	8.3	9.0	17
Zecer-56	8.4	9.0	16	8.4	8.8	16
ZZ	2.0	44.0	80	8.5	8.0	15
clinoptilolite	2.4	42.7	76	8.4	8.9	15
MZ	2.0	44.0	80	8.9	6.0	11
H.NZ-450	2.2	43.0	78	8.9	6.0	11
Zeben-06	8.0	11.0	20	9.3	3.9	7
NZ	3.9	39.4	61	-	-	-
Zemor-06	4.5	30.0	49	-	-	-
Zestec-06	8.0	11.0	20	-	-	-
Zeolite 4/20	0.1	5.5	8	-	-	-

In Table IV some results of ammonium elimination, at 25°C, by five products selected according Table III, in waters of different salinities, are shown.

Table V shows a resume of retention (%) by different products. In Table VI the maximum eliminations of every PZNs, according to different salinities, are indicated.

Our experiments have shown some levels of maximun eliminations depending on different water salinities: 20% of ammonium retention with the PZN named Zecer-56 in seawater, 32% with Zecer-56 in seawater 1,75% salinity, 68% with ZZ in domestic water, and 99% of ZZ in distilled water.

So, employing different PZNs, it is possible the treatment of wastewaters to reduce the ammonium concentration according to the salinity of contaminated waters.

Table IV: Ammonium retention by PZNs, in waters of different salinities, indicating final concentration of ammonium in solution (C_f, ppm), percentage of elimination (%) and retention (x.10^{-3} meq/g f PZNs)

PZNs	Solutes	C_f	%	x
Zeben-56	Distilled water	6,17	38,3	42,5
Zecer-56	DI	5,00	50,0	55,5
Zemor-06		0,17	98,3	100,0
Zenca-06		4,17	58,3	64,8
ZZ		0	99,0	100
Zeben-56	Domestic water	7,75	22,5	25,0
Zecer-56	DO	6,12	38,8	43,1
Zemor-06		1,63	83,7	93,0
Zenca-06		4,90	51,0	56,7
ZZ		1,22	87,3	97,5
Zeben-56	Seawater 1,75%	8,24	17,6	19,5
Zecer-56	1,75%	7,06	29,4	32,7
Zemor-06		7,25	27,5	30,5
Zenca-06		8,82	11,8	13,1
ZZ		6,08	39,2	43,5
Zeben-56	Seawater 3,5%	8,70	13,0	14,4
Zecer-06	3,5%	8,00	20,0	22,2
Zemor-06		9,00	10,0	11,1
Zenca-06		-	-	-
ZZ		8,6	14,0	15,6

Table V: Resume of ammonium retention (%) for five PZNs, in waters with different salinities.

	Salinities			
PZNs	DI	DO	1,75%	3,5%
Zeben-56	38,3	22,5	17,6	13,0
Zecer-56	50,0	38,8	29,4	20,0
Zemor-06	98,3	83,7	27,5	10,0
Zenca-06	58,3	51,0	11,8	-
ZZ	100,0	87,3	39,2	14,0

Table VI: Ammonium eliminations (%) by different PZNs, in media containing the studied salinities.

	Salinities			
PZNs	DI	DO	1,75%	3,5%
Zeben-56	-	-	-	-
Zecer-56	-	-	-	X
Zemor-06	X	-	-	-
Zenca-06	-	-	-	-
ZZ	-	X	X	-

Besides, the PZNs with large capacity of elimination contain heavy metal in their structures which may confirm the theory about the existence of linkings among zeolitic product, heavy metal and ammonium, for elimination of this cation.

References

[1] Ferreiro Almeda, Mª S., S. Ramos, J. López Ruiz and J.M. López Alcalá. 1998. New products of zeolitic nature with interest on marine systems. Cuadernos de Química Oceanográfica, 2: 27-44.

[2] -López Ruiz,J. 1982. Zeolites and ammonium in marine acuaculture. Diputación de Cádiz. Spain.

[3] López Alcalá, J.M. G. Rodríguez Fuentes and J.L. López Ruiz. 1998. Modification of a zeolite for improved ammoniun retention. IV Convegno Nazionale Scienza e Tecnologia delle Zeoliti. Universita A. Volta. Milano/Como. Italy.

[4] López Alcalá, J.M and López Ruiz, J. Elimination of ammonium in seawater by zeolitic products. 2001. Zeolites and Mesoporous Materials at the Down of the 21st Century. Elsevier. pg. 372.

[5] Rodríguez Fuentes, G, J.M. López Alcalá, J. Pérez Sánchez and J.L. López Ruiz. 1998. Retention of ammonium contained in sea water by a decationized cuban zeolite. Estudios de Biogeoquímica. Zona Costeira Ibérica. Universidade de Aveiro. p. 169.

[6] Mumptom, F.D. and P.H. Fishman. 1977. The application of natural zeolites in aquaculture. J.of Animal Science, 45(5): 1988.

[7] Strickland, J.D.H, and Parsons, T.R. 1972. A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada. Ottawa.