COLUMN LEACHING EXPERIMENTS
ON AMMONIUM CHARGED ZEOLITITE

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Abstract

Laboratory experiments were performed to evaluate the inorganic nitrogen leaching of NH_4-charged zeolitite (chabazite-bearing). Two columns, filled with zeolitite enriched in ammonium by mixing with swine manure and NH_4Cl solution, respectively, were flushed with synthetic rain water in saturated conditions. Ammonium content in the leachate solution of the first column was higher than that measured in the second column, but in both cases it represented less than 9% of the total exchangeable ammonium. A small amount of nitrate, deriving from the exchange method with manure, was also found in the first column. The quantity of ammonium remained in the zeolitite after leaching was determined via cation exchange with KCl. The results of this study suggest that the NH_4-charged zeolitite is only little affected by nitrogen leaching by rainfall and could be safely used as soil conditioner for agricultural purposes.
Keywords: *column leaching tests; ammonium charged zeolitite; cation exchange; swine manure*

Introduction

Natural zeolitites are rocks containing more than 50% of zeolites (Galli and Passaglia, 2011), a kind of minerals with peculiar physical and chemical properties, like high and selective cation exchange capacity (CEC), molecular absorption and reversible dehydration (Bish and Ming, 2001). The most common zeolitic species present in zeolitites are chabazite, heulandite–clinoptilolite, and phillipsite. In particular, the chabazite is the most commonly used natural ammonium exchanger (Passaglia and Laurora 2013; Leyva-Ramos et al. 2010; Lahav and Green 1998). Ammonium is an important source of nitrogen for many plant species and it is the main compound of nitrogen in manures. Livestock effluents, whose NH_4^+ concentration could exceed 1000 mg/l, are often used as fertilizers; it is known that intensive livestock breeding is one of the major sources of nitrogen pollution in water (Goldberg, 1989; Williams, 1995; Widory et al., 2004). When the NH_4^+ is not oxidized, (for example under anoxic conditions) it may reach dangerous concentrations in those areas where the natural background is already high for this cation (Di Giuseppe et al. 2013, 2014; Mastrocicco et al. 2013). In this respect, the

European Directive 98/83/CE sets to 0.5 mg/l the maximum ammonium concentration allowed in water for human use.

Once in the soil, ammonium is biologically transformed to nitrate (Rivett et al. 2008), a highly soluble N compound; high concentration of NO_3^- flowing into the water system can cause various environmental problems, mainly eutrophication phenomena.

Zeolites are capable to exchange ammonium from solutions and are frequently used in the treatment of wastewaters (Passaglia 2008). After saturation, zeolites are thrown away or regenerated, depending on the economic feasibility of N recovery. Several types of regeneration have been studied (Hedström 2001) and, indeed, many of them are very expensive. A very useful and ecologically valuable use of NH_4-charged zeolites is that proposed by ZeoLIFE project (LIFE+10 ENV/IT/000321), an Italian diagenized pyroclastic rock (ignimbrite) containing more than 60 wt% of chabasite zeolite and subordinate amounts of other minerals, is mixed with swine manure (an ammonium-rich solution) to create a NH_4-charged zeolitite (NH4CZ hereafter) that, added into the agricultural fields, sensibly decreases the need for fertilizers.

All traditional fertilizers, including those specifically manufactured to slowly release their nutrients, suffer from water leaching during rainfalls and/or irrigation activities (Badruzzaman et al. 2012; Snyder et al. 1984) The mineralogical characteristics of zeolites and their crystal-chemical properties make them a very promising tool for the controlled storage and release of ammonium (Gholamhoseini et al., 2013).

The main goal of this work is to study the leaching behaviour of NH_4^+ during the water–NH4CZ interaction. For this purpose, laboratory column experiments were used to evaluate the total amount of NH_4^+ released by NH4CZ after a long flushing of synthetic rain water (LT1). Considering that under oxidizing conditions and in presence of bacteria derived from the manure, the released ammonium may be converted to nitrate, NO_3^- was also measured after each test. The quantity of ammonium retained by the NH4CZ after the leaching test has also been determined (LT2). Furthermore, the leaching tests were repeated on a zeolitite exchanged with ammonium chloride, in order to check the possible behavioural differences between materials exchanged with poly-cationic (like swine manure) and mono-cationic solutions (LT3).

Materials and methods

Ammonium-enriched zeolitite from swine manure. NH_4CZ used in LT1 and LT2 (NH_4CZ-m) was obtained by mixing natural potassic chabazite zeolitite (Table 1) with swine manure in a specifically conceived prototype, under particular operative conditions (Coltorti et al., 2012). The starting material is a granular (Ø < 3 mm) by-product of the quarrying activity, air-dried before treatment. Its high Cation Exchange Capacity (CEC), low Na content and very high and constant Total Zeolitic Content (TZC), whose main species is represented by potassic Chabazite,

make it the most suitable material for ammonium exchange and a subsequent re-use for agricultural purposes.

OXIDE	wt%	MINERAL	wt%
SiO_2	51.6	chabazite	68.5 (0.9)
Al_2O_3	16.6	phillipsite	1.8 (0.4)
Fe_2O_3	3.38	analcime	0.6 (0.3)
TiO_2	0.48	**TZC**	**70.9**
P_2O_5	0.18	mica	5.3 (0.6)
MnO	0.11	k-feldspar	9.7 (0.7)
MgO	1.76	pyroxene	2.9 (0.4)
CaO	5.00	volcanic glass	11.2 (1.0)
Na_2O	0.79	**PHYSICAL PROPERTIES**	
K_2O	5.84	CEC (meq/g)	2.17
LOI	14.3	AD (g/cm^3)	0.87
SUM	100	WR (%)	48.4

Table 1

Major elements (oxides), mineralogical composition and main physical properties of zeolitite used in the prototype to obtain NH4CZ. Standard deviations are reported in parenthesis. **TZC**, *total zeolitic content; CEC, cation exchange capacity; AD, apparent density; WR, water retention.*

The prototype, located in an intensive swine breeding, collects swine manure from the upper layer of a big storage pool where the manure resides in open air conditions without any particular treatment. It is an unfiltered liquid with solid fraction of about 1wt %, high ammonium content and mildly alkaline pH (Table 2).

Solid %	< 1	Al	1.41
pH	8	K	1679
Fluoride	58.8	P	80.2
Chloride	1501	Ca	130
Nitrite	11.1	Ti	0.199
Bromide	6.05	V	0.025
Nitrate	42.7	Cr	0.079
Phosphate	136	Mn	0.773
Sulfate	8.59	Fe	4.50
NH_4	2128	Co	0.033
Li	0.026	Ni	0.122
B	2.11	Cu	0.531
Na	809	Zn	4.44
Mg	17.0	Sr	0.575

Table 2

Solid fraction (%), pH, and main anions and cations (mg/l) of swine manure used in the prototype to obtain the NH4CZ used in the leaching tests.

Ammonium-enriched zeolitite from ammonium chloride. NH4CZ used in LT3 (NH4CZ-c) has been obtained by mixing the same natural potassic chabazite zeolitite with a synthetic ammonium-rich (2000 mg/l) solution at the same operative conditions used in the prototype.

All leaching tests have been conducted at laboratory conditions (20°C) using polyethylene (PE) columns with an internal diameter of 2 cm and a length of 15 cm, equipped with PE pre and post-chambers, consisting of uniformly packed NH4CZ and a 50 μm Nitex mesh at both ends of the column, in order to avoid material losses. The arrangement of NH4CZ within the column took place in 15–20 increments, and each increment was lightly packed before placing the next one on top. For LT1 and LT3, the elution started with a slow saturation of the column with synthetic rain water (deionized water MilliQ plus $CaCl_2$ 0.01 mM, pH=7.5); the mixture was left still for one night in order to reach the equilibrium. After equilibration, the synthetic rain water was pumped through the column by a peristaltic pump with a constant flow rate of 4 ml/min; 51 pore volumes (20 ml each, for a total of 1.02 l/m^2) have been flushed and individually collected for analysis. At the end of LT1 experiment, the same column has been flushed with 0.5 l of a 1M KCl solution; the effluent was collected at fixed volumes for NH_4^+ measurements. The schematic diagram of the column experiments is shown in figure 1.
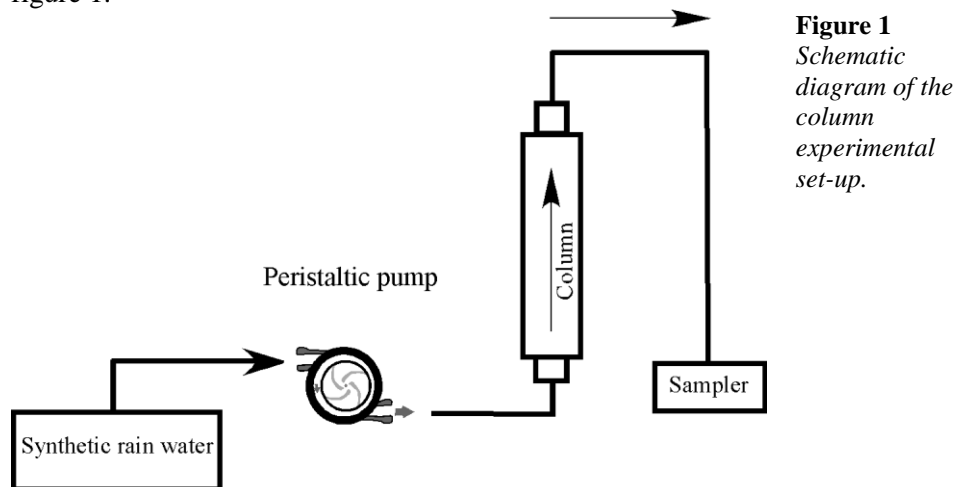

Figure 1
Schematic diagram of the column experimental set-up.

Exchangeable NH_4^+ content in NH4CZ-m and NH4CZ-c before column leaching tests (Table 3) has been measured via chemical extraction, by mixing 10 g of material with 100 ml of a 1M KCl solution for 1 hour; the supernatant has been separated with a Watman 20 μm filter. Ammonium concentration in the supernatant and in the leachate of NH4CZ-m and NH4CZ-c was measured with an ORION 95-12 gas-sensing electrode after conversion to ammonia. Two mL of ISA (Ionic Strenght Adjustor) were added to 100 mL of solution and standards immediately before each measurement. Calibration was carried out by single meter reading of two standards bracketing the expected sample range and differing in concentration by a factor of ten (these standard are obtained properly diluting a 1000 mg/L certificated ammonium standard solution). Calibration was verified every hour by placing the electrode in a fresh aliquot of the standard solutions; errors for each measurement were in the order of ± 2%.

NH_4^+ and NO_3^- concentration in the porevolumes has been determined with a CADAS 100 UV/Vis spectrophotometer (Hach-Lange, UK). Anions determination on manure have been carried out via a Dionex ICS-1000 ion chromatographer. Main cations and trace elements have been measured using a X Series Thermo-Scientific spectrometer ICP-MS. Chemical analysis of zeolitite samples was carried out via a wavelength-dispersive Philips PW 1480 X-Ray Fluorescence (XRF) spectrometer. An X'Pert PRO – PANAlytical diffractometer was employed to perform mineralogical quantitative phase analyses on zeolitites.

Results

Ammonium concentration decreases from 190 to 14.3 mg/l in the first 5 pore volume of LT1 (Fig. 2a, Table 3), then it reaches 7.5 mg/l after the remaining 46 pore volumes.
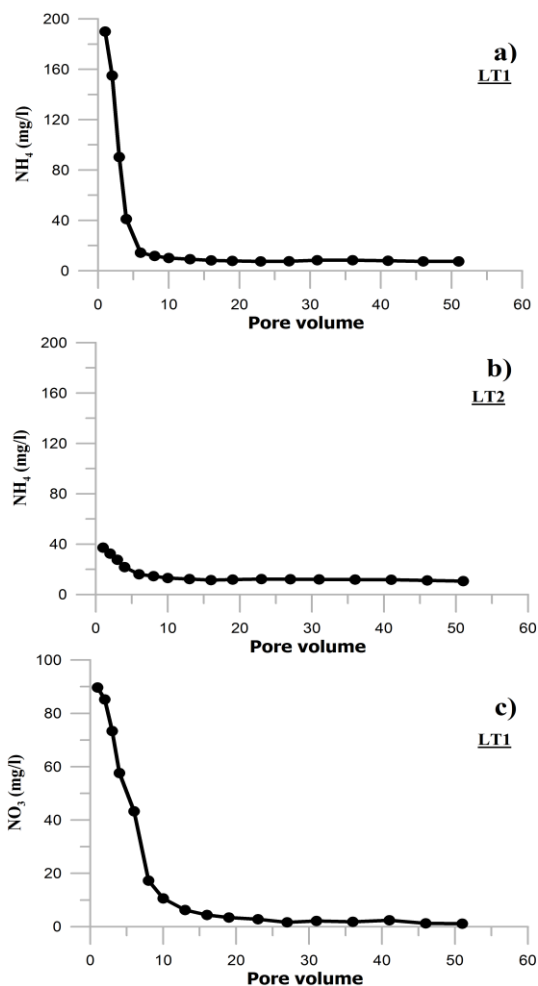

Figure 2
Plots for the NH4CZ-m (a, c) and the NH4CZ-c (b), which show ammonium and nitrate concentration variation versus pore volumes flushed.
2a, and b, ammonium concentrations in the leachate of LT1 and LT2, respectively; 2c, nitrate concentration in the leachate of LT1.

A similar trend has been observed in LT2, even if ammonium concentration in the first pore volume is lower than the correspondent LT1 pore volume (37.3 mg/l, Fig. 2b, Table 3). A total of 0.26 over an initial content of 2.95 mg of $N-NH_4^+$ per gram of zeolitite has been lost in LT1, corresponding to 8.7% of the initial exchangeable $N-NH_4^+$. On the other hand, 0.08 over a total of 9.42 mg/g of $N-NH_4^+$ have been lost in LT2; that is only the 0.8% of the total exchangeable $N-NH_4^+$. Theoretically, 2.69 and 9.34 mg/g of $N-NH_4^+$ should be retained in NH4CZ-m and NH4CZ-c, respectively. In LT1, a release of a small amount of $N-NO_3^-$ was also observed (0.05 mg/g, Fig. 2c, Table 3), whereas no NO_3^- has been found in LT2, as expected. During LT3, NH_4^+ concentration ranges from 1181 mg/l in the first 0.1 l of leachate, to 20 mg/l after 0.5 l of flushed solution (Fig. 3).
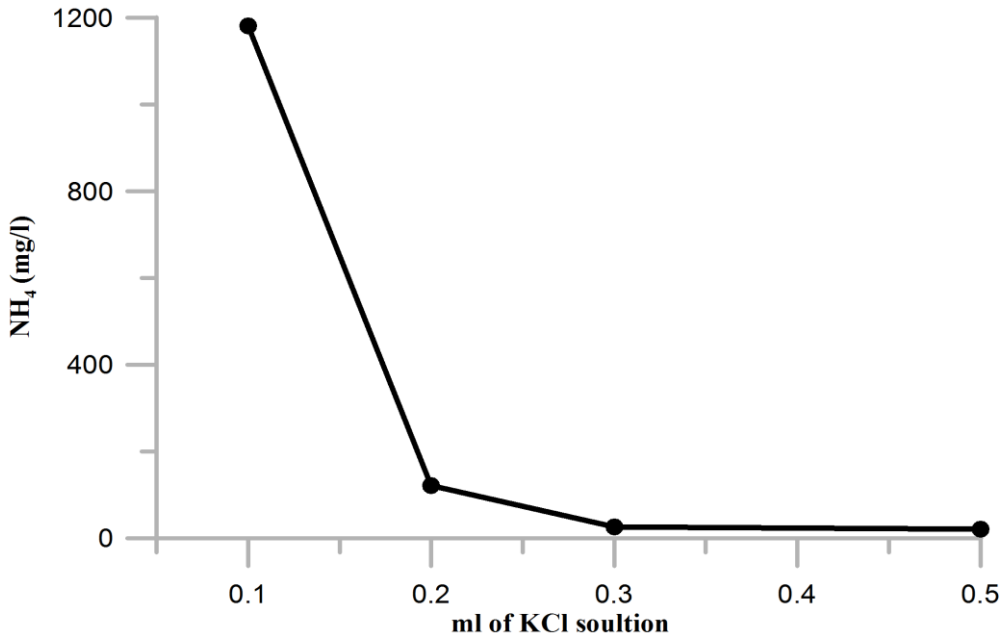

Figure 3. *Plot for the concentration of ammonium exchanged by NH4CZ-m compared to the volumes of potassium chloride flushed into the LT1.*

The total exchangeable $N-NH_4^+$ remained in the NH4CZ-m after a long leaching with synthetic rain water is of 2.87 mg/g, a value very close to the theoretical calculated from LT1 experimental results (Table 3).
The difference between the theoretic and the measured residual ammonium in NH4CZ-m is most probably due to the different extraction method used to determine the initial NH_4^+ amount (batch method), whose removal efficiency is lower than that of the column KCl leaching method used to determine the ammonium remained in the NH4CZ-m after LT1.

Table 3: *Leaching test Nitrogen balance. All values are mg of N per gram of zeolitite. Initial, N-NH$_4^+$ content gained during the charging process and determined by KCl extraction; Lost in 51 pore-volumes, N-NH$_4^+$ and N-NO$_3^-$ lost during leaching; Total N lost, total amount of N lost during the leaching by NH4CZ; Theor res, theoretic residual N-NH$_4^+$ after leaching; After exchange, real N-NH$_4^+$ still contained in the NH4CZ after the leaching and determined by KCl extraction.*

Sample	Initial	Lost in 51 pore-volumes		Total	Theor res	After exchange
	N-NH$_4^+$	N-NH$_4^+$	N-NO$_3^-$	N lost	N-NH$_4^+$	N-NH$_4^+$
NH4CZ-m	2.95	0.26	0.05	0.30	2.69	2.87
NH4CZ-c	9.42	0.08	0	0.08	9.34	

Discussion and conclusions

Notwithstanding the high number of flushed pore volumes, the total NH$_4^+$ released in both LT1 and LT2 is low. A remarkable difference can be envisaged between the first two tests, as NH4CZ-m loses an amount of ammonium almost an order of magnitude higher than NH4CZ-c (0.26 vs 0.08 mg/g, Table 3), under the same experimental conditions. Two possible explanations can be invoked: 1) NH4CZ-m has not been washed after the prototype treatment, and residual manure blobs and ganglia could be entrapped within the zeolitite porous matrix, whose composition probably included Ca and K salts. When NH4CZ-m came in contact with the synthetic rainwater these salts get solubilized, creating high cations local concentrations ,which enhanced the NH$_4^+$ exchange hosted in the chabasite. This phenomenon does not happen in the case of NH4CZ-c, where no salts are formed during its production. 2) using a mono-cationic NH4Cl solution, the charge distribution in the chabasite framework is more uniform than that resulting from the use of a poly-cationic solution like swine manure (Passaglia 2008); by consequence, the chabasite in NH4CZ-c is more stable and less prone to ammonium release during flushing.

The use of a mono-cationic solution to enrich zeolitite can also explain the higher amount of NH$_4$ trapped in NH4CZ-c with respect to NH4CZ-m (Table 3). When using manure, the zeolitite also exchanges other cations, like K and Ca, resulting in a lower total ammonium uptake (Passaglia 2008).

A certain amount of NO$_3^-$ was also detected in LT1. This N compound does not derive from a cation exchange (zeolites do not exchange negatively-charged ion or molecules), but most probably comes from the nitrification processes of the manure residua. In fact, an average of 43 mg/l of NO$_3^-$ was found in the manure used in the prototype (Table 2).

NH4CZ has been produced for its use as a soil conditioner capable to reduce N-leaching and to allow a considerable reduction of the fertilization. Previous greenhouse experiments in range of ZeoLIFE project established that 5-10 kg/m^2 (depending on soil grain size) of ammonium-enriched zeolitite were the right dose for a 50% reduction of fertilizers (Faccini et al. 2014). If 10 kg/m^2 are added, and hypothesizing a constant NH$_4^+$ content in the NH4CZ-m (2.95 mg/g, Table 3) and the amount of released NO$_3^-$ (0.05 mg/g, Table 3), a total of about 300 kg N/ha

would be input in the first 30 cm of soil, of which a maximum amount of 30 kg/ha could be leached in the porewater. This scenario, however, is theoretical and would be unlikely, due to the fact that leaching from rainfalls is different and lesser than what simulated in the laboratory column experiments. On the contrary, all traditional fertilizers, from urea 46% N to the slow-release forms, could be entirely leached with N losses ranging from 170 kg/ha to about 380 kg/ha or more, depending on the limitation in the agricultural N input established by the local law. Previous experiments (Faccini et al., 2013) showed that a soil fertilized with urea for a total of 260 kg N/ha (MAS for *Zea Mais L.*) released in the porewater an amount of nitrate more than double than what was found in a soil added with 7 kg/m^2 of NH4CZ-m, proving that almost the entire amount of the ammonium acquired during the treatment with swine manure is retained by the zeolitite and could be at plants' disposal. The use of ammonium-charged zeolitite in agriculture seems to be a promising method to reduce nitrogen leaching in the hydrologic system. Adding 5-10 kg/m^2 of NH4CZ-m to a soil would create a reservoir of exchangeable N capable to allow a reduction in the amount of fertilizers, thus contributing to further decrease the polluting potential of the cultivations, especially of those highly nitrogen demanding. Although, long term field results are still needed to proof and quantify the efficiency of this innovative technique to foster a more environmental friendly large scale agricultural management.

Acknowledgements

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EXPERIMENTATIONS EN COLONNE DE LIXIVIATION SUR ZÉOLITHITE CHARGÉE EN AMMONIUM

Résumé

Des expérimentations de laboratoire ont été effectuées pour évaluer la lixiviation de l'azote inorganique sur zéolithite (contenant chabazite) chargée en ammonium. Deux colonnes, rempli de zéolithite chargée en ammonium une par le contact avec le fumier de porc et l'autre avec une solution de NH_4Cl, ont été lixiviée avec de l'eau de pluie synthétique dans des conditions saturées. La teneur en ammonium dans la solution de lixiviation de la première colonne était supérieure à celle mesurée dans la deuxième colonne, mais dans les deux cas, il représentait moins de 9% de l'ammonium échangeable totale. Une petite quantité de nitrate, dû à la méthode d'échange avec du fumier, a également été trouvé dans la première colonne. La quantité d'ammonium resté dans la zéolithite après le lessivage a été déterminée par échange cationique avec KCl. Les résultats de cette étude suggèrent que le zéolithite chargée en ammonium est très peu affectée par le lessivage de l'azote par la pluie et peut être utilisé sans danger comme conditionneur de sol à des fins agricoles.

Mots clés: *tests de lixiviation colonne; zéolithite chargée en ammonium; échange de cations; fumier de porc*

ESPERIMENTI DI LISCIVIAZIONE IN COLONNA SU ZEOLITITI CARICATE IN AMMONIO

Riassunto

Al fine di valutare la lisciviazione di azoto da parte di una zeolitite (costituita da casite) caricata in ammonio, sono stati realizzati specifici test di lisciviazione. Due colonne, una riempita di zeolitite caricata in ammonio grazie al mescolamento con liquame suino, ed una tramite del clouro di ammonio, sono state flussate in condizioni satura con acqua di pioggia sintetica. L'ammonio nella soluzione lisciviante in uscita dalla prima colonna risulta maggiore rispetto alla seconda, ma in entrambi i casi esso è meno del 9% rispetto all'ammonio scambiabile totale. Una piccola quantità di nitrato, derivante dal metodo di scambio con il liquame suino, è stato trovato nella soluzione in uscita dalla prima colonna. La quantità di ammonio che è rimasto nella zeolitite dopo lisciviazione è stata determinata mediante scambio cationico con KCl. I risultati di questo studio, suggeriscono che la zeolitite carica con ammonio è poco influenzata dalla lisciviazione delle piogge e potrebbe essere tranquillamente utilizzata come ammendante in agricoltura.

Parole chiave: *test di lisciviazione in colonna; zeolitite carica in ammonio; capacità di scambio cationico; liquame suino*