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Ammonium-exchanged zeolitite preparation for agricultural uses: from laboratory tests to large-scale application in ZeoLIFE project prototype

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Abstract

Water nitrate pollution is one of the biggest environmental issues in all those Countries whose economy is largely based on agriculture. Limiting the nitrogen compound input in the soil-water-air system requires the development of innovative and sustainable farming practices, allowing the reduction of fertilizer amounts but assuring good yields. This study describes the optimization of the uptake of swine manure-derived ammonium by zeolitite, as one of the first result of ZeoLIFE project ("Water pollution reduction and water saving using a natural zeolitite cycle", LIFE+10 ENV/IT/000321). Natural Italian chabazite-bearing zeolitite has been mixed with swine manure at different zeolitite/manure ratios and operative conditions, in a series of laboratory batch tests. The effective NH_4^+-uptake has been measured with different methods, in order to validate the best criteria to reproduce the cation exchange reaction at large scale in a prototype, specifically conceived and built for the industrial production of NH_4^+-charged zeolitite.

Experimental results indicate that the best conditions for maximum ammonium uptake are matched using a zeolitite/manure ratio of 25 g/L, a stirring time of 45 minutes and a resting time of 12 hours. These experimental conditions, when operatively applied at the prototype, always led to a good absorption of ammonium, although appreciably less than that obtained in laboratory tests. The obtained material has been spread into an agricultural field, where an increase of the yield has been obtained notwithstanding a significant reduction of the chemical fertilization.

Key words: Zeolitite; Ammonium; CEC; Swine manure; Fertilizer; Prototype.

Introduction

Agriculture remains one of the main source of water pollution, and farmers need to adopt more sustainable practices, as huge efforts are still required in order to restore optimal water quality across the European Union (EU). Generally, farming is responsible for the major N-compound discharges into surface waters and groundwater, and still nowadays agricultural practices in all Europe use a large amount of chemical fertilizers and animal manure, with large regional differences (Velthof et al., 2014). Of the total nitrogen input in the fields, a large amount is actually not absorbed by the crops and resides in the soil (Mastrocicco et al., 2013; Wang et al., 2013a; Sebilo et al., 2013), where it could be converted into highly soluble nitrates and flushed away into the water system (Arbat et al., 2012; Aschonitis et al., 2012; Wick et al., 2012; Wang et al., 2013b), triggering different degenerative processes and ultimately causing eutrophication phenomena (Del Amo et al. 1997; De Wit et al., 2005; Statham, 2012). Moreover, when denitrification processes occur in soils (Rivett et al., 2008), greenhouse gases are released into the atmosphere (Benbi, 2013; Skinner et al., 2014). 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) and it heavily contributes to greenhouse gases (like CO_2 and methane) emissions worldwide (FAO, 2006). With the Nitrates Directive (91/676/EC) and the Water Framework Directive (WDF 2000/60/EC) the EU aimed at preventing nitrate pollution by promoting the use of good farming practices and established a protocol for water protection and management, reporting measures that must be taken by each Member State to reduce dumping and toxic substance emissions, favor the restoration of hydrologic resources and reach a good chemical and ecological state of waters. All EU States have drawn up action programs, and by 2010 about 40% of the territory is subject to their implementation.

Natural zeolitites are rocks containing more than 50% of zeolites (Galli and Passaglia, 2011), a kind of minerals with peculiar physical and chemical properties, as high and selective cation exchange capacity (CEC), molecular absorption and reversible dehydration (Bish and Ming, 2001). Zeolites have a complex three-dimensional, negatively charged tecto-silicatic structure (framework) with large, cage-like cavities interconnected through channels, that are able to accommodate K^+, Na^+, Ca^{2+} or other cations, water and even small organic molecules. Cations are only weakly connected to the framework and can migrate in and out of the zeolite structure; they can be released partly or totally when the mineral comes in contact with a solution from which, in turn, the zeolite extracts an equivalent amount of other cations. Thanks to their high CEC and remarkable selectivity for cations characterized by low ionic potential (NH_4^+, K^+, Pb^{2+}, Ba^{2+}; Passaglia, 2008), zeolites are capable to uptake ammonium from solutions in various environments (Passaglia and Laurora, 2013) and then to release it under proper conditions. Thus, the use of natural zeolitites in environmental protection is progressively increasing, and they have been used for the treatment of sewage waters, to remove ammonium and to amend greenhouse substrates and agricultural soils (Ming and Allen, 2001; MO2013A000354).

In this context, ZeoLIFE project (LIFE+10 ENV/IT/000321) has been conceived to test an innovative integrated zeolitite cycle aiming at reducing the ammonium content in livestock effluents and correcting agricultural soils, with improvement of the yield and economization of fertilizers and water for irrigation, ultimately leading to a reduction of fresh and groundwater pollution and excessive exploitation of the water resource.

This study describes the optimization of swine manure-derived ammonium uptake by zeolitite, as the first result of ZeoLIFE project. Natural chabazite-bearing zeolitite from a quarry in the Central Italy (Malferrari et al., 2013) has been mixed with swine manure at different zeolitite/manure ratios and operative conditions, in a series of laboratory batch tests. The effective NH_4^+-uptake has been measured with different methods, in order to validate the best criteria for the reproduction of the charging process at large scale in a prototype, specifically conceived and built at the project pilot site for the industrial production of the NH_4^+-charged zeolitite.

Materials and Methods

Materials

Batch experiment apparatus. The selected zeolitite comes from a zeolitized pyroclastic deposit quarried in a particular lithostratigraphic unit of the Sorano Formation (the so-called Lithic Yellow Tuff body) where K-Chabazite is the overall prevalent zeolite specie. For its detailed mineralogical and chemical characterization see Malferrari et al. (2013). The Sorano Formation is part of phonolitic-tephritic ignimbrite with black pumices deposits, erupted during Quaternary by the volcanic complexes of Bolsena, Vico and Bracciano lakes (Passaglia et al., 1990). These rocks underwent extensive zeolitization in a sort of natural autoclave environment ("geoautoclave"; Passaglia and Vezzalini (1985), (and references therein), thanks to the activity of pore fluids heated by the thermal energy of the pyroclastic deposit itself. This peculiar phenomenon is at the base of the very fine grain size of the zeolites and their homogeneous distribution within the rock, as well as the prevalent mineral type and its composition reflect the low Na/K and Si/Al ratios of the original volcanic glass and the pH of the circulating pore waters (Passaglia and Vezzalini, 1985; Passaglia et al., 1990). The thickness of these pyroclastic deposits (up to 80 m), their widespread occurrence (the sole Sorano quarry has an extension of 60,000 m^2) and the high zeolitic content make them an exploitable resource from the economical point of view.

Exchange experiment between zeolitite and manure were carried out using a granular (Ø = 0.2-3 mm) byproduct of the quarrying activity, in static mode (Vassileva and Voikova, 2009), being this one the most suitable method for large-scale reproduction in a prototype.

The main goal was to determine the interaction conditions that allow the maximum ammonium uptake by the zeolitite. This result does not necessarily coincide with the maximum reduction of ammonium in manure, as it is strictly related to the amount of added zeolitite. Thus several exchanging experiments (Figure 1, in supplementary material) were performed varying the zeolitite/manure ratio, the stirring and resting times (i.e., the amount of time during which the zeolitite remains still in contact with the manure after stirring). Taking into account the potential operating capacity of the prototype for large-scale production, 25 and 75 grams per liter of manure have been respectively selected as the minimum and maximum amounts of zeolitite used in the laboratory tests. Each exchange experiment was performed in triplicates at room conditions with a fixed volume (1 L) of manure. After stirring, during the resting period, small aliquots (i.e., 5 mL) of manure were sampled at increasing intervals of time, properly diluted, and characterized for residual ammonium content. At the end of the resting period, the zeolitite has been separated from the slurry with a 250 µm filter, washed with distilled water and air dried. Both manure and zeolitite have been chemically characterized for main ions contents. An outline of manure and NH_4^+-charged zeolitite (NH4CZ hereafter) samples prepared in laboratory is shown in Table 1.

Prototype for large scale NH4CZ production

The prototype (Figure 1) is composed by a 2.2

Table 1. Manure and zeolitite samples after laboratory experiments.

Zeolitite / manure ratio (g/L)	Stirring times (min)	Resting time before manure sampling (hrs)	Last manure samples labels	NH4CZ samples labels
25	15	4, 8, and 12	M-25-15-12	25-15-12
50			M-50-15-12	50-15-12
75			M-75-15-12	75-15-12
25	30		M-25-30-12	25-30-12
50			M-50-30-12	50-30-12
75			M-75-30-12	75-30-12
25	45		M-25-45-12	25-45-12
50			M-50-45-12	50-45-12
75			M-75-45-12	75-45-12

Stirring times indicate times under which zeolitite samples were kept in contact with manure under continuous stirring. Resting times indicate the lapses of time of static interaction before manure sampling for ammonium analysis and, in text and figures, is indicated by the last number of each label (for example, in Figures 2 and 3, label M-25-45-8 identifies a manure sample from a batch with zeolitite/manure ratio of 25 g/L, stirred for 45 minutes and sampled after 8 hours of static contact with the zeolitite). Last manure samples are those selected for main ions content determinations (see Table 2). NH4CZ are zeolitite samples separated from manure after the highest resting time (i.e., 12 hours), washed with deionized water and air dried.

m (ø) x 5.3 m (h) main tank for the swine manure storage (about 10 m^3), with 2 inflow and 2 outflow valves. The loading of swine manure is performed using a 30 m^3/h pumps (Pmax = 1.5 bar) for the transport of the liquid fraction from the storage pool. Zeolitite can be introduced from the top into the vessel by a motorized pulley. The tank is equipped with a vertical mixer (mechanical stirrer) regualted with a timer, with a top speed of 300 m^3/h for the mixing of zeolitite and manure. After interaction, the manure can be discharged into a drain well. For recovery of the NH_4^+-charged zeolitite, the treated material is discharged opening the ball valve at the bottom of the tank. A 250 μm-sieving vibrating system may be, optionally, inserted at the bottom of the vessel to separate the different particle size of NH4CZ.

The prototype, that is located in Codigoro (Ferrara, Italy) near ZeoLIFE experimental field described in Malferrari et al. (2013), Mastrocicco et al. (2013) and Di Giuseppe et al. (2014), processes the same swine manure and zeolitite

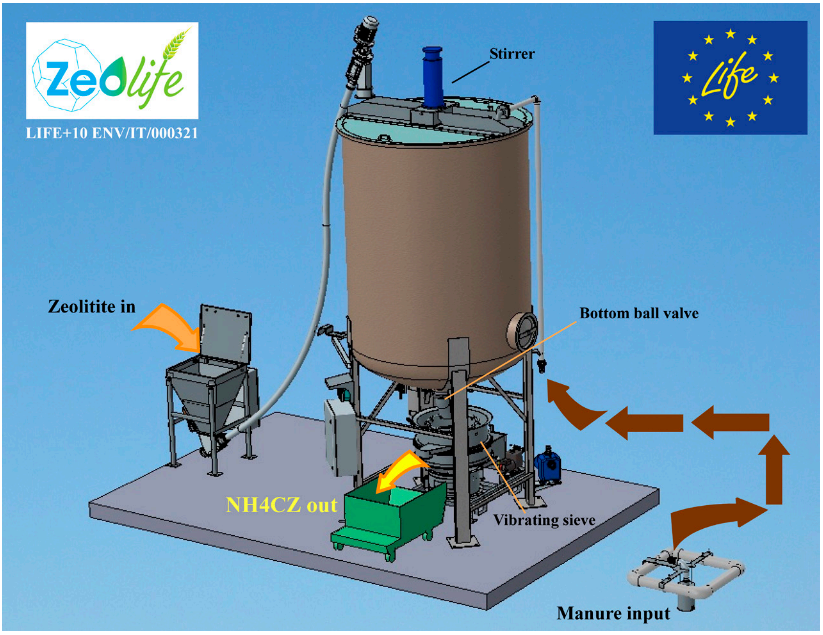

Figure 1. Sketch of the prototype® for zeolitite treatment with swine manure.

used in batch experiments. Manure ammonium content has been regularly measured before and after each treating cycle with a gas-sensing electrode probe installed in situ, after conversion to ammonia. Anion and trace element contents have been analyzed on a sub set of representative samples collected during the whole length of prototype activity period.

The mechanical features of the prototype and the application of the operating conditions optimized with the laboratory test allowed to obtain, on average, up to 500 Kg/day of NH4CZ. A selection of prototype NH4CZ samples (labeled as PRT-1-PRT-9), collected weekly after appropriate quartering for a period of about two months, have been gathered for this study.

Main anions and cations determination on manure

The swine manure used in the batch experiments is a low density (1 gr/cm^3) liquid with a solid fraction lesser than 1%. EC and pH are, on average, 21 mS/cm and 8.0, respectively. Main ions content for manure samples before and after treatment with zeolitite used in each exchange experiments is reported in Table 2. F^-, Cl^-, $(NO_2)^-$, Br^-, $(NO_3)^-$, $(PO_4)^{3-}$, and $(SO_4)^{2-}$ measurements have been carried out via a Dionex ICS-1000 ion chromatographer. Manure samples were conveniently diluted and put in 5 mL test tubes sealed with a cap equipped with a 0.22 μm filter. The tubes are put in an AS-40 Dionex automatic sampler where an injection pump extracts the solution that passes through the filter and is conveyed to the mixing chamber. Quality Control (QC) samples were run every 10 samples and the standard deviation for all QC samples run was better than 4%.

Na^+, K^+, Ca^{2+}, Mg^{2+} have been measured using a X Series Thermo-Scientific ICP-MS spectrometer. Manure samples were diluted in

Table 2. Main ions concentration in manure before and after treatments with zeolitite.

Ions concentration (mmol/L)

	MANURE (*)	M-25-15-12	M-50-15-12	M-75-15-12	M-25-30-12	M-50-30-12	M-75-30-12	M-25-45-12	M-50-45-12	M-75-45-12
F^-	2.71	2.55	2.25	1.17	1.39	1.56	1.57	1.40	1.40	1.49
Cl^-	41.2	46.6	42.7	41.7	43.4	40.6	40.4	42.2	42.4	43.3
$(NO_2)^-$	0.213	0.220	0.197	0.128	0.220	0.226	0.219	0.201	0.194	0.211
Br^-	0.065	0.083	0.073	0.064	0.065	0.076	0.072	0.072	0.066	0.070
$(NO_3)^-$	0.005	0.008	0.030	0.004	0.004	0.004	0.009	0.003	0.002	0.011
$(PO_4)^{3-}$	1.37	1.09	0.918	0.778	0.823	0.499	0.265	0.816	0.637	0.535
$(SO_4)^{2-}$	0.138	0.574	0.109	0.233	0.923	0.174	0.125	0.086	0.113	0.172
Na^+	34.5	32.9	33.8	31.4	33.0	33.0	33.1	32.7	34.7	38.8
K^+	42.0	43.4	40.3	36.1	41.0	39.6	41.6	41.2	40.3	46.2
Ca^{2+}	3.53	6.05	11.65	4.61	4.35	7.02	7.02	6.14	5.90	5.85
Mg^{2+}	0.75	0.86	1.16	0.71	0.89	1.20	0.84	1.06	1.34	1.08
NH_4^+	109	91.6	91.0	75.7	87.6	91.7	80.4	80.3	92.1	91.9

(*) Average composition of ten manure analyses before treatment with zeolitite.

deionized water at 1:50; 10 mL of the diluted solutions were put in test tubes for automatic sampling. Specific amounts of Rh, In and Re were added to the analyzed solutions as an internal standard, in order to correct for instrument drift. Accuracy and precision, based on replicated analyses of samples and standards, are better than 10% for all elements, well above the detection limit. Reference standards (ESL1, EUL1, ref) were also analyzed to cross-check and validate the results.

Ammonium measurements

Ammonium in manure 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 all manure samples (after proper dilution) 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 standards 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%. Additional information on the adopted analytical techniques are reported in the supplementary information SI-1.

Ammonium absorbed by zeolitite was

determined both in solution after proper selective chemical extraction, and directly on solid via thermogravimetric measurement coupled with evolved gases mass spectrometry.

Chemical extraction and gas-sensing electrode (GSE) measurements. Five grams of each NH4CZ sample were put in centrifuge tubes, added with 50 mL of a 1N NaCl solution, stirred at 640 rpm on orbital stirrer for 15 minutes, and then allowed to rest for other 15 minutes. The obtained suspension was subsequently centrifuged at 5000 rpm for 3 minutes. The supernatant was carefully poured off into a PVC container. The last bit of supernatant was removed with a pipet tip, and the container was properly sealed. This procedure was repeated three times, thus obtaining a total of 150 mL of supernatant for each starting NH4CZ sample. The sealed containers were stored in a refrigerator at 4 °C. Since a slight turbidity of suspension does not affect the ammonium measurement, samples needed neither distillation nor filtration. Ammonium measurements were done following the same procedure as previously described for manure.

The cation exchange capacity is usually measured employing cesium as exchange cation. In this research, however, we preferred to use sodium essentially for two reasons: i) chabazite has a high affinity for sodium; ii) a purpose of the project is to parallel as much as possible the reactions that could occur in the soil of ZeoLIFE project experimental field, where the porewater may have high sodium concentrations (Di Giuseppe et al., 2014).

Thermogravimetric measurement (pyrolytic extraction). Thermogravimetry (TGA) allows the determination of the mass as a function of temperature or time; this thermal technique provides information concerning thermal stability and composition of the sample and of any intermediate compound which may be formed. When these measures are combined with chemical analysis of evolved gases, it is possible to determine the reactions that are at the base of each thermal effect. In particular, it is possible to estimate the amount of absorbed ammonium by evaluating the variation of mass in correspondence with the release of NO_3^- derived from the oxidation of NH_4^+ by the oxygen present in the furnace atmosphere.

Pyrolytic extraction of absorbed ammonium is more far-reaching than a chemical extraction; however, as a result of a possible partial overlapping of contiguous thermal reactions, it cannot be excluded that the extraction via pyrolysis involves a small overestimation.

Before thermal measurement, zeolitite samples have been powdered (grain size less than 2 micron). Thermo gravimetric curves were obtained using a Seiko SSC 5200 equipped with TG/DTA 320U Module and the gas mass spectrometer GeneSys Quadstar 422. The experimental conditions were: Heating rate: 10.0 °C/min; Heating range: 25-900 °C; Data measurement: every 0.5 sec; Purging gas: helium/oxygen (90/10) at a flow rate of 100µL/min; DTA reference: calcinated kaolinite; Mass analyses: in multiple ion detection mode scan on m/z=14, 16, 17, 18, 28, 30, 32, 44, 46, where m/z is the ratio between selected AMU and charge; AMU integration time: 1 sec; Detector current: 1100V both on SEM and FARADAY. Further information are reported in the supplementary information SI-2a.

Chemical analyses of zeolitites

Chemical analysis of zeolitite samples after treatment with manure was carried out on pressed pellets of powdered rock via a wavelength-dispersive Philips PW 1480 X-Ray Fluorescence (XRF) spectrometer, using the methods of Franzini et al. (1975) and Leoni and Saitta (1976) for the determination of element concentration. Fe was assumed to be in its trivalent oxide form. As Loss On Ignition (LOI), the values determined via thermogravimetric measurements were considered. Chemical and mineralogical compositions of natural zeolitite are reported in Malferrari et al. (2013).

Results and Discussion

Batch experiments

Ammonium measurements in manure. Results of batch experiment are reported in Figures 2

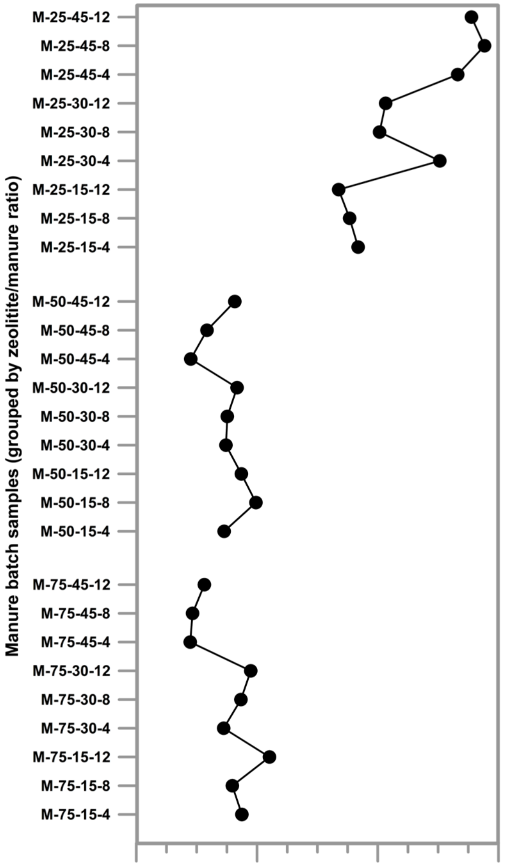

Figure 2. Absorbed ammonium in zeolitite after batch experiments, as determined from the difference in ammonium content of swine manure before and after treatment. Samples are grouped by zeolitite/manure ratio. The numerical code of sample labels indicates respectively zeolitite/manure ratio, stirring time and resting time.

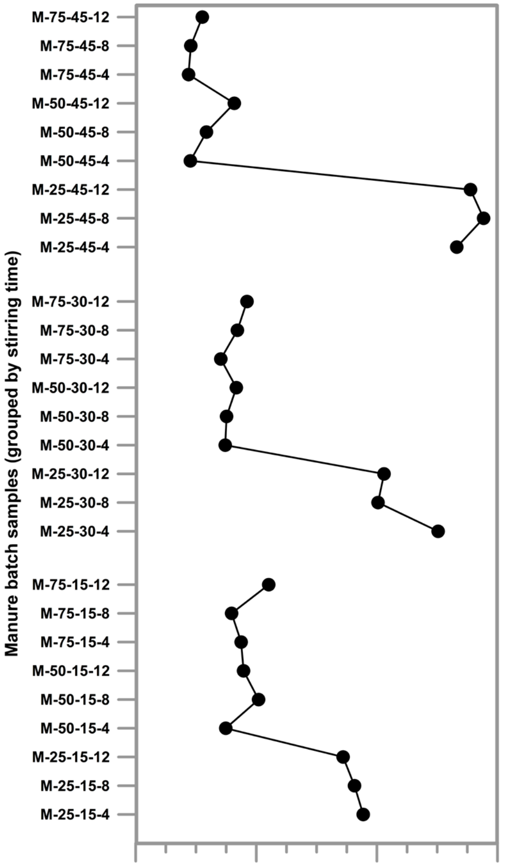

Figure 3. Absorbed ammonium in zeolitite after batch experiments, as determined from the difference in ammonium content of swine manure before and after treatment. Samples are grouped by stirring time. The numerical code of sample labels indicates respectively zeolitite/manure ratio, stirring time and resting time.

only in the case of 45 minutes of treatment, and, additionally, it seems to greatly facilitate the absorption only in the case of low zeolitite/manure ratio (Figure 3), iii) the resting time does not really affect the absorption, since the measured variations frequently fall within the experimental error. The most relevant outcome, however, is that there is no linear relationship between zeolitite/manure ratio and amount of absorbed ammonium: in fact, the use of 50 or 75 g/L of zeolitite does not cause significant differences in absorption in spite of a greater reduction of ammonium concentration in manure when using 25 g/L.

Main ions measurements in manure. Main anions and potential exchangeable cations in manure before and after laboratory experiment are reported in Table 2. Noticeable variations in Na^+, K^+, Ca^{2+} and Mg^{2+} concentrations in manure are in relation with the exchange reactions that occur between manure and zeolitite; however, no correlation between their changes in concentration can be found, thus suggesting that exchange mechanisms are complex and not modelizable in this environment. A decrease in the most abundant cations in the manure, coupled with an increase in the less concentrated can overall be envisaged in the post-treatment liquid (Figure 4a).

Regarding the anions (Figure 4b), fluorides show a general decrease which is, generally, higher when longer stirring times are used; phosphate reduction is in close correlation with both stirring time and zeolitite/manure ratio (Figure 5) and, in particular, it is favored by low zeolitite/manure ratios. It is noteworthy that nitrites and nitrates concentrations are very low and similar at the beginning and at the end of the experiments, which means that all the ammonium missing in the liquid has been taken up by the zeolitite and not been oxidized. No correlation can be found for chlorides and sulphates concentrations.

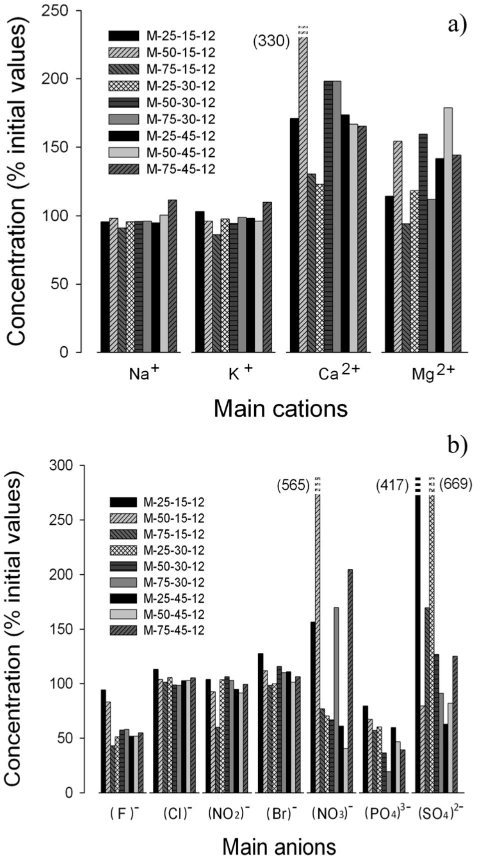

Figure 4. Main cations (a) and anions (b) concentration in manure samples from the laboratory batch experiments after the maximum resting time (12h).

Ammonium measurements on NH4CZ (chemical and pyrolytic extraction). As already stated, NH_4^+ absorbed by zeolitite can be estimated both as the NH_4^+ released when the NH4CZ interacts with a solution containing cations (e.g., Na^+) that can substitute, via cation exchange mechanism, the absorbed NH_4^+ in zeolitite, and as the amount of ammonium released in a well-defined thermal range (see also supplementary information SI-1 and SI2b).

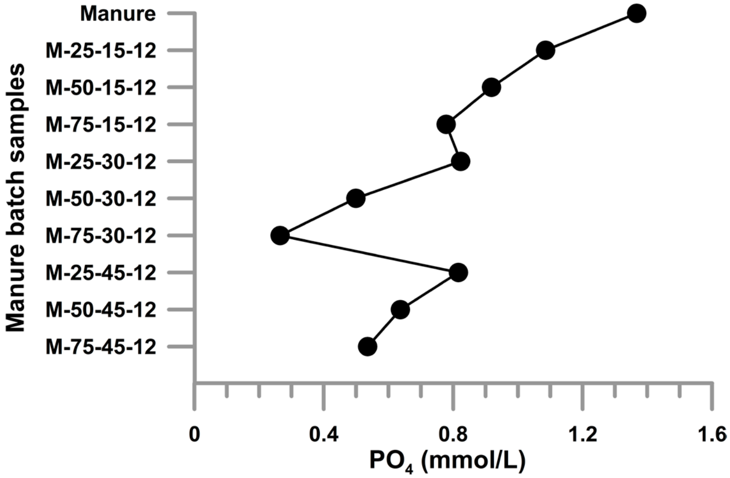

Figure 5. $(PO_4)^{3-}$ concentration in manure samples from the laboratory batch experiments after the maximum resting time (12 h). Samples are grouped by stirring time.

Results of chemical and pyrolytic extraction are reported in Table 3.

The amount of ammonium determined via pyrolytic extraction is always greater than the amount detected via chemical extraction, as a result of both the partial overlap of the thermal decomposition reactions and the increased efficiency of the heating process with respect to the chemical extraction. Actually, an average of the two values can be considered a reliable result. In contrast, it is often found a mismatch between the measurements performed on manure after treatment with the zeolitite and the measurements on the corresponding NH4CZ samples, in particular when referring to the samples obtained using a zeolitite/manure ratio of 25 g/L.

Chemical characterization of zeolitite after treatment. The results of chemical analysis via X-ray fluorescence on natural zeolitite and after treatments are shown in Table 4. Variations measured on major elements fall within the variations ranges of natural zeolitite, as also documented in Malferrari et al. (2013), and therefore can be considered as negligible the effect of leaching during the exchange with manure. This conclusion is also supported by quantitative mineralogical analysis on zeolitite after treatment, that does not detect substantial changes (supplementary information SI-3). A sensible variation of the exchangeable cations Na^+, K^+, Ca^{2+} and, to a lesser extent, Mg^{2+}, can be envisaged. In particular, all NH4CZ samples show a slight increase in Mg^{2+} and a reduction of the others afore mentioned elements. In the manure, by contrast, a corresponding trend of variation of these cations cannot be found, with the only exception of Ca^{2+} (Table 2, Figure 4a). Phosphorous content variations are concordant, as it decreases in manure and increases in zeolitite. Since a direct interaction (e.g., absorption) between phosphorus and minerals contained in zeolitite is not possible, the increase in the solid fraction is likely due to precipitation of compounds of this element, maybe induced by the interaction between manure and zeolitite and/or by biologically

Table 3. NH4 measurements (mmol/g) in NH4CZ samples determined via chemical (GSE) and pyrolytic (TGA) extraction.

SAMPLE	GSE	TGA	MANURE	AVG M/Z (S.D.)	% NomCEC
25-15-12_R1	0.37	0.39			
25-15-12_R2	0.40	0.51			
25-15-12_R3	0.39	0.43			
Average (R1-R3)	0.38	0.44	0.69	0.51	23.3
ST. DEV (R1-R3)	*0.01*	*0.05*		*0.16*	
50-15-12_R1	0.38	0.44			
50-15-12_R2	0.37	0.45			
50-15-12_R3	0.35	0.47			
Average (R1-R3)	0.37	0.45	0.36	0.39	18.0
ST. DEV (R1-R3)	*0.01*	*0.01*		*0.05*	
75-15-12_R1	0.31	0.38			
75-15-12_R2	0.29	0.38			
75-15-12_R3	0.28	0.32			
Average (R1-R3)	0.29	0.36	0.44	0.37	16.8
ST. DEV (R1-R3)	*0.01*	*0.03*		*0.07*	
25-30-12_R1	0.49	0.47			
25-30-12_R2	0.47	0.43			
25-30-12_R3	0.46	0.44			
Average (R1-R3)	0.47	0.45	0.85	0.59	27.2
ST. DEV (R1-R3)	*0.01*	*0.02*		*0.22*	
50-30-12_R1	0.45	0.57			
50-30-12_R2	0.41	0.53			
50-30-12_R3	0.41	0.55			
Average (R1-R3)	0.42	0.55	0.34	0.44	20.2
ST. DEV (R1-R3)	*0.02*	*0.02*		*0.10*	
75-30-12_R1	0.34	0.47			
75-30-12_R2	0.36	0.44			
75-30-12_R3	0.36	0.48			
Average (R1-R3)	0.35	0.46	0.38	0.40	18.4
ST. DEV (R1-R3)	*0.01*	*0.02*		*0.06*	
25-45-12_R1	0.47	0.62			
25-45-12_R2	0.43	0.58			
25-45-12_R3	0.53	0.66			
Average (R1-R3)	0.48	0.62	1.14	0.75	34.3
ST. DEV (R1-R3)	*0.04*	*0.03*		*0.35*	
50-45-12_R1	0.33	0.49			
50-45-12_R2	0.39	0.44			
50-45-12_R3	0.32	0.49			
Average (R1-R3)	0.35	0.47	0.33	0.38	17.7
ST. DEV (R1-R3)	*0.03*	*0.02*		*0.08*	
75-45-12_R1	0.28	0.39			
75-45-12_R2	0.28	0.38			
75-45-12_R3	0.36	0.46			
Average (R1-R3)	0.31	0.41	0.23	0.31	14.5
ST. DEV (R1-R3)	*0.04*	*0.04*		*0.09*	

MANURE reports the NH4 concentration in zeolitite determined as the amount of NH4 subtracted from manure after 12 hours of resting time; AVG-M/Z is the average (with Standard Deviation in italic) of NH4 concentrations measured via EGA, TGA and from manure; %NomCEC is the percentage of the nominal C.E.C. (i.e., 2.17 mmol/g -Malferrari et al. 2013) accomplished with the experiments and calculated with respect to AVG-M/Z values. R1-R3 are the three replicates.

Table 4. Major elements (oxide weight %) in NH4CZ samples obtained in the laboratory experiments. Each value is the arithmetic mean of three replicates; standard deviation (S.D.) is reported in italic.

OXIDE	Natural zeolitite	*S.D.*	25-15-12	*S.D.*	25-30-12	*S.D.*	25-45-12	*S.D.*	50-15-12	*S.D.*
SiO_2	51.60	*0.350*	53.30	*0.591*	54.00	*0.295*	54.00	*0.005*	53.90	*0.310*
Al_2O_3	16.60	*0.356*	17.30	*0.192*	17.60	*0.096*	17.60	*0.002*	17.50	*0.101*
Fe_2O_3	3.38	*0.095*	3.53	*0.039*	3.58	*0.020*	3.58	*0.000*	3.58	*0.021*
TiO_2	0.48	*0.031*	0.47	*0.005*	0.47	*0.003*	0.47	*0.000*	0.47	*0.003*
P_2O_5	0.18	*0.012*	0.21	*0.014*	0.22	*0.013*	0.22	*0.012*	0.22	*0.012*
MnO	0.11	*0.006*	0.11	*0.001*	0.12	*0.001*	0.12	*0.000*	0.12	*0.001*
MgO	1.76	*0.184*	1.78	*0.026*	1.80	*0.019*	1.80	*0.012*	1.80	*0.021*
CaO	5.00	*0.151*	2.93	*0.037*	2.97	*0.019*	2.97	*0.010*	2.97	*0.016*
Na_2O	0.79	*0.030*	0.27	*0.004*	0.27	*0.003*	0.27	*0.002*	0.27	*0.002*
K_2O	5.84	*0.122*	4.94	*0.057*	5.01	*0.028*	5.01	*0.005*	5.01	*0.027*
LOI	14.30	*0.762*	15.20	*0.862*	14.00	*0.517*	14.00	*0.089*	14.10	*0.505*
SUM	100.00		100.00		100.00		100.00		100.00	

OXIDE	50-30-12	*S.D.*	50-45-12	*S.D.*	75-15-12	*S.D.*	75-30-12	*S.D.*	75-45-12	*S.D.*
SiO_2	53.80	*0.176*	54.00	*0.249*	54.20	*0.297*	54.10	*0.310*	54.0	*0.239*
Al_2O_3	17.50	*0.057*	17.60	*0.081*	17.6	*0.097*	17.60	*0.101*	17.6	*0.078*
Fe_2O_3	3.57	*0.012*	3.58	*0.017*	3.59	*0.020*	3.59	*0.021*	3.58	*0.016*
TiO_2	0.47	*0.002*	0.47	*0.002*	0.47	*0.003*	0.47	*0.003*	0.47	*0.002*
P_2O_5	0.22	*0.012*	0.22	*0.011*	0.22	*0.012*	0.22	*0.011*	0.22	*0.011*
MnO	0.12	*0.000*	0.12	*0.001*	0.12	*0.001*	0.12	*0.001*	0.12	*0.001*
MgO	1.80	*0.017*	1.80	*0.017*	1.81	*0.020*	1.81	*0.020*	1.80	*0.017*
CaO	2.96	*0.011*	2.97	*0.008*	2.98	*0.017*	2.97	*0.008*	2.97	*0.007*
Na_2O	0.27	*0.002*	0.27	*0.002*	0.27	*0.002*	0.27	*0.001*	0.27	*0.002*
K_2O	4.99	*0.015*	5.010	*0.019*	5.030	*0.027*	5.02	*0.024*	5.02	*0.018*
LOI	14.30	*0.321*	14.00	*0.352*	13.70	*0.434*	13.80	*0.464*	13.90	*0.378*
SUM	100.00		100.00		100.00		100.00		100.00	

induced chemical precipitation (Bortone et al., 1992) and variations in the oxidation-reduction potential (Obaja et al., 2003).

Prototype production

The laboratory experiments were aimed at determining the interaction conditions between zeolitite and manure leading to the maximum ammonium uptake by the zeolitite. Absorbed ammonium measurements carried out both on manure and NH4CZ samples after laboratory treatments indicate that a zeolitite/manure ratio of 25 g/L, a stirring time of 45 minutes and a rest time of 12 hours are the most suitable conditions to achieve the goal; thus these "optimized" parameters were paralleled at the prototype. Each cycle employed 250 Kg of zeolitite and 1 x 10^4 L of manure; prototype activity started at the beginning of April and went on until October 20th, 2012, with an average of one cycle per day. Due to the cold temperatures and unfavorable weather, the production has been stopped during winter and resumed in the middle of April 2013. At the end of May, the in-situ gas-sensing electrode probe required maintenance and ammonium and nitrate measurements started again in July; the production went on until the middle of October 2013, for a total NH4CZ amount of 87 tons.

Ammonium content in manure before treatment can vary mainly in dependence of temperature, the amount of liquid stored in the basin, and the quantity of water used to wash the pigpens (in the operative period we found values ranging from 530 to 2560 mg/L, Figure 6), thus the ammonium decrease in manure after each treating cycle can vary a little. An average decrease of 203 mg/L and of 251 mg/L in the operative periods of 2012 and 2013 has been respectively obtained. Other variable affecting ammonium uptake can also be ascribed to operative conditions such as exact the correct weighting of zeolitite (250 ± 5 Kg) as its relative humidity that can slightly vary in function of the atmospheric conditions (the zeolitite was stored in open-air conditions).

Nitrate contents in the manure used in the prototype are higher than those found in manure used in the batch experiments, being on average 41 mg/L in 2012 and 93.8 mg/L in 2013. Since the source is the same, the difference is most probably due to the suction method employed to transfer the liquid from the storage basin to the tank, which implies a partial oxygenation of the manure. NO_3^-, however, cannot be exchanged with zeolitite; in-situ denitrification processes (Bortone et al., 1992) can explain the average manure nitrate concentrations of 36.8 and 73.5 mg/L found after prototype treatment in 2012 and 2013, respectively.

Periodic measurements on NH4CZ samples obtained at the prototype are reported in Table 5. As anticipated, the measurement reported here are related to a selection of samples (PRT-1-PRT-9) produced in about two months of prototype activity. In order to make measurements as homogenous as possible, all the samples, before characterization, were air dried under the same conditions of humidity and temperature; washing with distilled water has not been performed.

The effective ammonium absorption in zeolitite after treatment with manure (Table 5a) was lower than those registered during batch experiments at the same experimental conditions. It may also be noted that the difference between the measurements performed on NH4CZ samples via chemical and pyrolytic extraction is not only less marked than in batch experiments, but a reversal of the trend (on average) can be envisaged.

As far as major elements (Table 5b) are concerned, like in the case of laboratory experiment, an increase of phosphorus compared to the natural zeolitite can be observed in NH4CZ samples, indicating the probable precipitation of phosphates. The differences concerning exchangeable cations

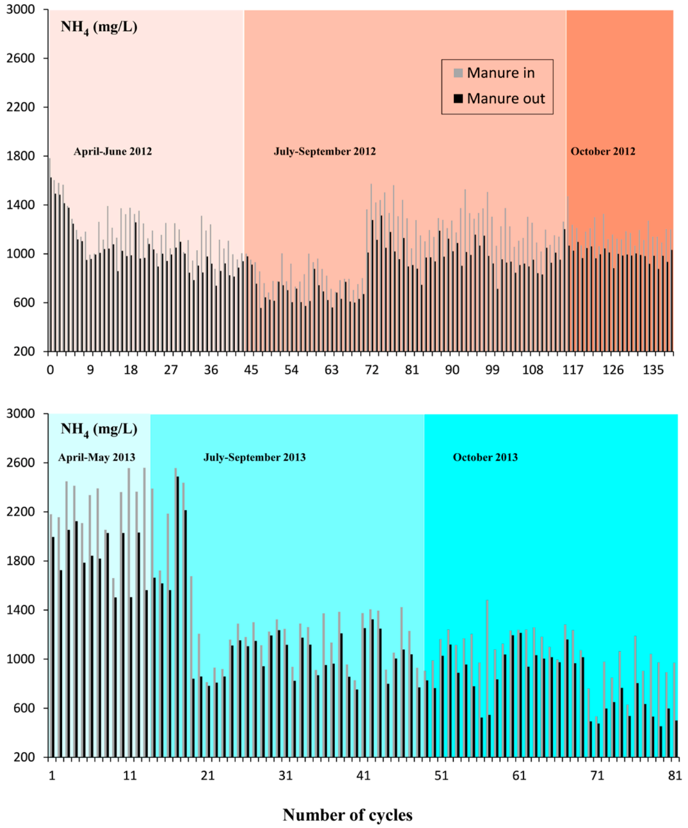

Figure 6. NH$_4^+$ contents in manure before anf after each treatment cycle in the prototype during 2012 and 2013 working period. Histrograms refear to the data-log file of the in situ probe and, for ease of reading, are reported in mg/L.

Table 5a. NH$_4^+$ measurements (mmol/g) in NH4CZ samples obtained at the prototype determined via both chemical (GSE) and pyrolytic (TGA) extraction. Each value is the arithmetic mean of three replicates; standard deviation (S.D.) is reported in italic.

	PRT-1	PRT-2	PRT-3	PRT-4	PRT-5	PRT-6	PRT-7	PRT-8	PRT-9	AVERAGE	25-45-12
GSE	0.39	0.43	0.39	0.41	0.57	0.39	0.42	0.40	0.42	0.43	0.48
S.D.	0.042	0.025	0.038	0.020	0.042	0.043	0.029	0.018	0.063		0.04
TGA	0.37	0.38	0.40	0.49	0.37	0.56	0.38	0.33	0.37	0.40	0.62
S.D.	0.004	0.007	0.008	0.001	0.007	0.037	0.013	0.044	0.083		0.03
AVGVAL	0.38	0.41	0.40	0.45	0.47	0.48	0.40	0.36	0.40		

AVGVAL is the average value between GSE and TGA measurements. AVERAGE is the average value among all NH4CZ samples here reported. For direct comparison is reported NH4 concentration of the laboratory sample 25-45-12 like in Table 3.

Table 5b. Major elements (oxide weight %) in NH4CZ samples obtained at the prototype. Each value is the arithmetic mean of three replicates; standard deviation (S.D.) is reported in italic.

	PRT-1	*S.D.*	PRT-2	*S.D.*	PRT-3	*S.D.*	PRT-4	*S.D.*	PRT-5	*S.D.*	PRT-6	*S.D.*	PRT-7	*S.D.*	PRT-8	*S.D.*	PRT-9	*S.D.*	AV.	*S.D.*	25-45-12	*S.D.*	Nat. Zeo	*S.D.*
SiO_2	53.80	*0.123*	53.80	*0.069*	53.70	*0.112*	53.90	*0.172*	53.10	*0.121*	53.40	*0.179*	53.70	*0.199*	53.80	*0.229*	54.20	*0.197*	53.70	*0.299*	54.00	*0.005*	51.60	*0.350*
Al_2O_3	17.50	*0.040*	17.50	*0.023*	17.50	*0.036*	17.50	*0.056*	17.30	*0.039*	17.40	*0.058*	17.50	*0.065*	17.50	*0.075*	17.60	*0.064*	17.47	*0.097*	17.60	*0.002*	16.60	*0.356*
Fe_2O_3	3.56	*0.008*	3.57	*0.005*	3.56	*0.007*	3.57	*0.011*	3.52	*0.008*	3.54	*0.012*	3.56	*0.013*	3.56	*0.015*	3.60	*0.013*	3.56	*0.020*	3.58	*0.000*	3.38	*0.095*
TiO_2	0.47	*0.001*	0.47	*0.001*	0.47	*0.001*	0.47	*0.002*	0.47	*0.001*	0.47	*0.002*	0.47	*0.002*	0.47	*0.002*	0.47	*0.002*	0.47	*0.003*	0.47	*0.000*	0.48	*0.031*
P_2O_5	0.22	*0.012*	0.22	*0.012*	0.23	*0.012*	0.23	*0.005*	0.23	*0.009*	0.23	*0.010*	0.21	*0.011*	0.21	*0.012*	0.22	*0.009*	0.22	*0.009*	0.22	*0.012*	0.18	*0.012*
MnO	0.11	*0.000*	0.12	*0.000*	0.11	*0.000*	0.12	*0.000*	0.11	*0.000*	0.11	*0.000*	0.11	*0.000*	0.11	*0.000*	0.12	*0.000*	0.11	*0.001*	0.12	*0.000*	0.11	*0.006*
MgO	2.06	*0.129*	1.93	*0.071*	1.79	*0.047*	1.79	*0.026*	1.57	*0.048*	1.83	*0.039*	1.83	*0.040*	1.91	*0.045*	1.88	*0.033*	1.84	*0.133*	1.80	*0.012*	1.76	*0.184*
CaO	3.26	*0.011*	3.11	*0.011*	2.96	*0.015*	2.97	*0.012*	2.14	*0.011*	3.02	*0.014*	3.02	*0.012*	3.02	*0.015*	3.06	*0.014*	2.95	*0.316*	2.97	*0.010*	5.00	*0.151*
Na_2O	0.27	*0.003*	0.27	*0.002*	0.27	*0.003*	0.27	*0.002*	0.19	*0.002*	0.27	*0.002*	0.27	*0.002*	0.27	*0.002*	0.27	*0.002*	0.26	*0.027*	0.27	*0.002*	0.79	*0.030*
K_2O	4.99	*0.013*	4.99	*0.009*	4.99	*0.014*	5.00	*0.017*	3.96	*0.013*	4.96	*0.018*	4.98	*0.018*	4.98	*0.022*	5.03	*0.019*	4.88	*0.346*	5.01	*0.005*	5.84	*0.122*
LOI	13.80	*0.290*	14.10	*0.113*	14.50	*0.187*	14.20	*0.260*	17.40	*0.186*	14.80	*0.124*	14.4	*0.075*	14.20	*0.137*	13.50	*0.130*	14.54	*1.131*	14.00	*0.089*	14.30	*0.762*
SUM	100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00				100.00	

AVERAGE is the average value among all NH4CZ samples here reported. For direct comparison are reported elements concentrations both of the laboratory sample 25-45-12 and natural zeolitite like in Table 4.

are less evident, with the exception of potassium that underwent a higher degree of exchange in comparison to the treatments at laboratory scale.

Main considerations

The main aim of batch experiments was to find the best parameters, in terms of zeolitite/manure ratio, stirring and resting time, to produce a zeolitite as much as possible rich in ammonium. As already stated by Malferrari et al. (2013), the nominal CEC of the selected zeolitite for ammonium is of 2.17 mmol/g. Since manure is a poly-cationic solution, a much lower operational CEC was expected, due to the competition between ammonium and other cations (approximately, 1/5 of the nominal CEC, also in consideration of what reported in Hedström, 2001); despite this, in all the experiments where a zeolitite/manure ratio equal to 25 g/L has been used, the amount of absorbed ammonium in manure indicated a CEC (Table 3) higher than the expected operative CEC (i.e., about 0.4 mmol/g). The apparent "extra-load" can be explained if a correction for the nitrogen loss by evaporation is supposed and applied. Nitrogen evaporation could have been enhanced during the experimental runs both by the stirring and the ventilation of the laminar flow hoods; however it can be roughly considered equal for each replicate and each run, due to the relatively small differences in the stirring time in comparison with the length of the resting, and being the flow hoods always working during all the experiments. This conclusion is supported also by measurements on NH4CZ samples, showing a smaller gap between measured and nominal CEC.

Treatment with slurry does not cause substantial variations in the quantitative mineralogical composition of the zeolitite (supplementary information SI-3). By contrast, the it affects significantly the zeolitite chemical composition, especially concerning the exchangeable cations. However, it should be pointed out that, at least for calcium, the measurements may be influenced by the precipitation of calcium phosphates, and through XRF analysis it is not possible to discriminate the calcium fixed in the structural channels of the zeolite from that precipitated as "external" phase. We can suppose, in fact, that phosphorous in manure tends to combine with the Ca made available by the zeolitite, to form either mono-, or di-, or more likely tri-calcium phosphates. Being mostly insoluble (?1<-log (K_{ps}) < ~30), these compounds precipitates together with the zeolitite during the resting phase, as supposed by Lai and Eberl (1986) and recently reported by Karapınar (2009). In consideration of our final purpose (soils amendment), this phenomenon, if verified, can be considered greatly promising since phosphate creates a pool of phosphorus for plants growth (Antoniadis et al., 2012).

Regarding the differences detected between the measurements of ammonium in zeolitite, it is significant that there is a marked difference only when considering the two series (i.e., GSE and TGA) of measurements of batch experiment samples, whereas the differences between the prototype samples are less pronounced. Prototype samples differ from batch experiment samples because: i) after the treatment they were not washed and ii) they were left in air (i.e., accumulated in the storage box) for at least 24 hours before being selected. The lack of washing should have caused a greater mass variation (relative to the thermal extraction of ammonium) in the samples from the prototype, but (on average) the opposite have been observed. Although the differences involved are modest, these findings leave an uncertainty on the correct assessment of the actual amount of ammonium absorbed by the NH4CZ. As far as author's knowledge is concerned, and with the exception of the NIST Ammonium ZSM-5 (which, however, is related to a synthetic zeolite), there is no cerificated standard for natural zeolitite exchanged with ammonium to be used to make a comparison.

Beside this, the overall analysis of the experimental results seems to indicate that, when operating conditions developed in the laboratory are paralleled at the prototype, the efficiency is lower (i.e., a minor amount of ammonium is absorbed by zeolitite, Table 5a). This outcome, however, was expected since it was reasonable to assume that the physical interaction between manure and zeolitite obtained in the batch experiments on small amounts of suspension can be paralleled at the prototype, but not exactly replicated.

The cation exchange capacity of the zeolitite largely depends on the content of zeolitite added to the solution: a low value of zeolitite/manure ratio determines a low daily production of zeolitite with a high NH_4^+ content; conversely a high value of the ratio allows a greater production of zeolitite with low content of ammonium. The experiments optimized the best working conditions in order to allow NH4CZ production at large scale. To achieve this goal it would have been counterproductive to test ratios lower than 25 g/L and greater than 75 g/L since in the first case, the operating potential of the prototype would have been underperformed, whereas, in the second case, a zeolitite with an ammonium content too low for agricultural purposes would have been produced.

The differences between some of the measured parameters, in terms of exchanged cations, are not strictly relevant for the ultimate goal of manufacturing a zeolitite enriched in ammonium to be used as a good soil conditioner. The NH4CZ obtained through the prototype treatment bears 0.40-0.43 mmol/g of ammonium (Table 5a), which means an average of 9.6 g of nitrogen per each Kg of material; when added into an agricultural soil at an amount $\geq$ 50 ton/ha, it supplies 480 kg or more of nitrogen, allowing a considerable reduction of the fertilization (up to 70% depending on the kind of crop). NH4CZ do not suffer ammonium leakage in consequence of rainfalls and/or irrigation (Colombani et al., 2014), so that the total amount of nitrogen input in an agricultural field thanks to the addition of NH4CZ is theoretically at crop’s disposal, as testified by several studies on greenhouse tests (Passaglia, 2008 and references therein), and by the results of the first year of experimental cultivation at ZeoLIFE experimental field (Faccini et al., 2014). Of course, the possible range of variation of ammonium content have to be taken into consideration when the mass balances between nitrogen added to the soil and nitrogen detected in porewater and groundwater will be carried out as a task of ZeoLIFE project.

Conclusions

Laboratory batch experiments for ammonium exchange between natural chabazite-zeolitite and swine manure resulted in a maximum uptake using a zeolitite/manure ratio of 25 g/L, 45’ of stirring time and a optimal resting time variable between 8 and 12 hours. These conditions have been successfully applied in a prototype tank for large scale production of NH4CZ to be added in an experimental agricultural field. Prototype NH4CZ contains an average of 0.41 mmol/g of ammonium, and the treatment favours the precipitation of phosphorus in the residual solid, making it a corrective capable to allow a reduction in the amount of NPK fertilizers.

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