Research Article

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Characterization of natural Yemeni zeolites as powder sorbents for ammonium valorization from domestic waste water streams using high rate activated sludge processes

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Abstract

BACKGROUND: In this study three natural Yemeni zeolites (NZ1, NZ2 and NZ3) having major minerals such as clinoptilolite and mordenite, were evaluated as low cost sorbents for the removal and recovery of ammonium ions.

RESULTS: The zeolite samples, with $pH_{PZC} = 9.1 \pm 0.2$, 7.9 ± 0.2 and 7.4 ± 0.2 for NZ1, NZ2 and NZ3, respectively, showed high ammonium sorption capacities. At pH 8, for treated waste waters: (i) with low NH_4^+ levels (from 25 to 100 $mgNH_4/L$); and (ii) for concentrated NH_4^+ side streams generated from the anaerobic digestion of sewage sludge (from 400 up to 1500 $mg\ L^{-1}$), maximum loading capacities of 27 to 51 $mgNH_4\ g^{-1}$ were measured for the studied zeolites. Measured sorption isotherms, in the concentration range 0.05 to 5 $g\ L^{-1}$, were well described by the Langmuir isotherm. The ammonium sorption kinetics was controlled by particle diffusion and was well described by both the homogeneous diffusion (HPDM) and shell progressive (SPM) models.

CONCLUSION: Comparison of the equilibrium data with results for natural and synthetic zeolites demonstrate the higher performance of the studied zeolites providing low residual ammonium values <1 $mgNH_4\ g^{-1}$ and <10 $mgNH_4\ g^{-1}$ when treating both diluted and concentrated-NH_4^+ streams, respectively.
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Supporting information may be found in the online version of this article.

Keywords: natural Yemeni zeolite; clinoptilolite; mordenite; ammonium recovery; high rate activated sludge

INTRODUCTION

Natural zeolites have attracted significant interest over the last two decades especially with regard to their capacity to eliminate or reduce water pollution problems. Nitrogen (N) is the primary element of plant and animal proteins and is essential to all life forms.[1] However, high concentrations of N in surface and ground water cause high oxygen demand and can lead to eutrophication.[2] Ammonium (NH_4^+) with NO_3^-/NO_2^- are the main inorganic ionic form of N present in domestic and industrial waste waters but it is also generated from organic N compounds.[3] In these types of effluents, the N forms are removed traditionally by biological methods[4] whereby the N is converted to biomass or is transformed into N_2 (g), although when biomass is anaerobically digested to produce bio-methane, N is again re-mineralized to NH_4^+.[5] However, new valorization technologies for the removal and recovery of ammonium are needed to overcome problems that could be encountered in: (a) the implementation of high rate activated sludge (HRAS) or up-concentration schemes promoting the enhancement of energy recovery by anaerobic digestion, producing treated effluents with high ammonium contents (up to 100 mg L^{-1});[6,7] (b) new stringent regulation of N levels on the discharges of

treated water (e.g. values of NH_4^+ below 1 mg L^{-1}); or (c) the need to recover nitrogen on account of its high nutrient value. Among the newer valorization strategies used is the recovery of ammonium as struvite; however, only a small fraction of the total ammonium load is recovered (c. 10%).[8,9] Alternative recovery strategies employ the use of striping and sorption processes, however increasing effort is being used on the integration of membrane processes.[10,11] The use of conventional synthetic polymeric sorbents (e.g. cation exchange resins) and polymeric membranes based technologies has limited applications mainly on account of the fouling encountered due to the high content of total suspended solids and

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dissolved organic matter present in waste waters.[11,13] Inorganic materials like ceramic membranes of zeolites represent a suitable option for promoting ammonium recovery mainly on account of their favorable physico-chemical properties.[14] However, there is a lack of study on whether zeolites could be integrated using standard sorption technologies like bed columns and granular forms[15,16] or whether they could be used as powdered forms in hybrid sorption-filtration technological approaches.[17–19]

Zeolite, which is a naturally occurring hydrated aluminosilicate mineral, mainly consists of a three-dimensional framework bearing tetrahedral structures of SiO_4 and Al_2O.[20,21] The cages and channels within the three-dimensional framework of the zeolites are occupied by water, alkali (Na^+, K^+) and alkaline earth cations (Ca^{2+}, Mg^{2+}, Ba^{2+}).[22–24] As these ion-exchangeable cations are present in hydrated forms in the zeolite cavities their exchange leads to the reformation of the pore structure.[23–25] Natural zeolites are very effective in the removal of ammonium, which occurs by exchange with Na^+, K^+, Ca^{2+} and Mg^{2+} as has been demonstrated in numerous studies of different mineral deposits.[26,27] The purification of waters and the treatment of industrial and urban waste waters have been the main fields of application of natural zeolitic materials.[28–30] From the large list of zeolite deposits identified and reported the most widely studied are those from Turkey, Slovakia, Australia, Greece, Iran and Italy.[31–33] However, limited studies could be found in relation to the Yemen which has huge reserves of zeolitic tuffs deposits which could have potential industrial and environmental applications.

Thus the objective of this study is two-fold: (a) to characterize mineralogically and chemically three different selected samples of zeolitic material obtained from three different deposits in Yemen, the selection was performed, inside a collaborative project between two geological research groups of Yemen and Tunisia; and (b) to determine the ammonium sorption properties of the zeolitic materials in powdered form for their ultimate use in the recovery of ammonium from treated waste waters by evaluating their equilibrium and kinetic parameters. Synthetic and real ammonium solutions were used for this characterization. Treated waste water used in the present study was collected from El Prat Waste Water Treatment Plant (Barcelona, Spain) and was found to contain common cations like calcium (200 mg L^{-1}), magnesium (74 mg L^{-1}), sodium (280 mg L^{-1}) and potassium (38 mg L^{-1}) and anions like chloride (1180 mg L^{-1}), phosphate (33 mg L^{-1}), and sulfate (45 mg L^{-1}). Such competing ions may affect NH_4^+ sorption. Finally, a detailed comparison of the properties of Yemeni zeolites was made with those of zeolites reported in the literature and widely used for industrial and environmental applications, especially for ammonium removal technology for new waste water treatment processes incorporating high rate activated sludge schemes.

MATERIALS AND METHODS

Yemen natural zeolites: sampling locations
Natural zeolites of good quality occurring in altered volcanic tuffs were identified in several areas of Yemen. The main reserves of high quality zeolite deposits are located in three provinces: Taiz, Ibb and Dhamar according to the Yemen Geological Survey and Mineral Resources Board.[34] Samples used in the present study were collected from three different locations: Jebel Hilen Maireb (Natural zeolite sample 1: NZ1), Jebel Hadad (NZ2) and Jebel el Hard (NZ3). Location details of the sample points are given in Fig. 1.

Zeolites physico-chemical characterization
Determination of crystal structure and the mineralogy of the zeolites was performed using X-ray diffraction (XRPD) D8 Bruker with Cu–k$\square$ ($\square$= 0,154) radiation operating at 40 kV and 40 mA. The chemical composition of the samples was analyzed by X-ray fluorescence (ARL 9900 X-ray). Sample morphology and surface chemical composition were analyzed by field emission scanning electron microscope (FESEM) (JEOL JSM-7001F) coupled to an energy dispersive spectroscopy (EDS) system (Oxford Instruments X-Max). Each FESEM image is originated from a different area of the sample, in order to ensure the homogeneity of the zeolitic structure. Qualitative and quantitative mineralogical characteriza- tion was carried out by means of X-ray powder diffraction patterns using a PanalyticalX'Pert Pro diffractometer equipped with a RTMS detector. Before all analyses, samples were ground and sieved by a particle size siever and thoroughly washed with de-ionized water to remove dust and traces of soluble particles.

The point of zero charge (PZC) was determined by the pH drift method.[34] A fixed amount of 0.2 g of sample zeolite was equilibrated in 50 mL of deionized water, 0.01 mol L^{-1} and 0.05 mol L^{-1} NaCl solutions (pH from 2 to 12) for 24 h under gentle agitation and at 22 ± 1 °C. The final pH was measured and the PZC was determined as the pH at which the addition of the sample did not induce a shift in the pH. The common intersection point (CIP) method was also used.[35] PZC experiments were performed in triplicate and the average data reported.

Ammonium equilibrium and kinetic batch studies
Batch equilibrium sorption experiments were carried out using standard batch methodology described elsewhere.[36] Fixed volumes (25 mL) of prepared ammonium (N) aqueous solutions in polyethylene tubes were used. They were shaken overnight with weighed amounts of dry zeolitic samples (particle size <200 $\square$m) using a continuous rotary mixer. Three different types of experi- ment were conducted: (a) sorption capacity as a function of ammo- nium concentration: in which 0.2 g of zeolite samples were added to varying ammonium (10−2000 mg-N/L) aqueous solutions main- tained at fixed pH using pH adjustment to achieve values of 8.0 ± 0.2; (b) sorption capacity as a function of equilibrium pH range: in which 0.2 g of NZ sample was added to fixed ammonium (600 mg-N/L) aqueous solutions and adjusting pH from 7 to 10 (using 0.1 mol L^{-1} HCl/NaOH); and (c) finally sorption capacity as a function of the amount of natural zeolite at a constant ammonium concentration (from 0.2 to 1 g in 25 mL of waste water solution). In all experimental conditions, samples were shaken for at least 24 h at 22 °C.

Batch kinetic sorption experiments were performed by adding 0.2 g of NZs in solutions containing 864 mg-NH_4 L^{-1} and shaken at 200 rpm. Tubes were withdrawn sequentially at given time intervals. All tests were performed in triplicate at 300 rpm and room temperature (22 ± 1 °C), and the average data reported. The samples were centrifuged for 10 min and then filtered using 0.45 $\square$m cellulose nitrate membrane. The total concentration of ammonium ions in the initial and in the remaining aqueous solution was determined.

Ammonium batch desorption studies
Samples of NZs (particle size <200 $\square$m) were saturated in 25 mL of solution containing 630 mg-NH_4 L^{-1} at 300 rpm for 24 h. NZ

samples were separated by filtration and rinsed several times with deionized water for the desorption experiment. The desorption

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Figure 1. Geographical location of zeolite deposits used in the present study: Jebel Hilen Maireb (Natural zeolite sample 1: (NZ1), Hadad (NZ2) and Jebel al Hard (NZ3).
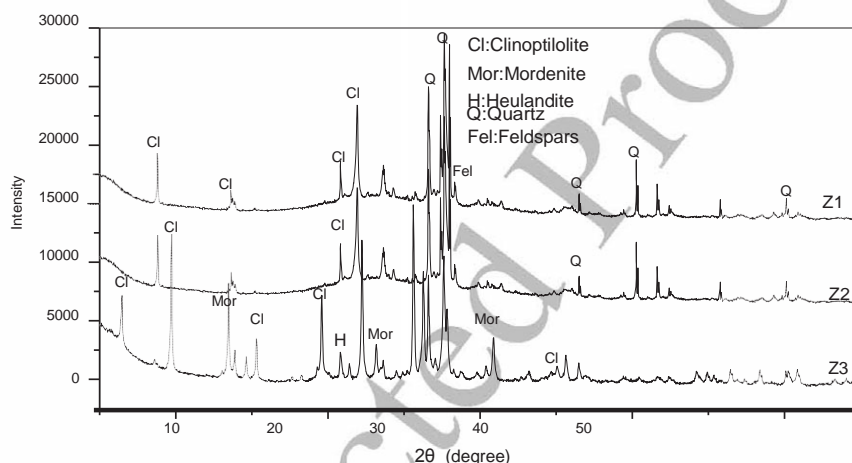

Figure 2. XRD patterns of Yemeni raw natural zeolites NZ1, NZ2 and NZ3 *(Cl (clinoptilolite), Mor (mordénite), H (heulandite), Q(quart), Fel(feldspars))*.

studies were performed by adding 0.2 g of the saturated zeolite into 25 mL of elution solution at 300 rpm for 20 h. 0,02 mol L^{-1} NaOH, 0.1 mol L^{-1} NaCl, 0.02 mol L^{-1} NaOH and 0.1 mol L^{-1} NaCl solutions were evaluated as desorbing solvents. After elution and proper conversion to the Na form the zeolite was washed water to remove the excess of the regenerant solution. Tests were performed in triplicate at 22 ± 1 °C, and average data reported. Anions and cation concentrations were determined by ionic chromatography (Dionex ICS-1100 and ICS-1000).

Loaded and desorbed zeolite samples were analyzed by XRD and samples were dried, avoiding high temperatures to minimize the potential losses of ammonium and ammonia.

Data treatment procedures
Ammonium sorption isotherms
Ammonium sorption values (q_e) were calculated from the batch experiment results using Equation (2):

$$q_e = \frac{(C_o - C_e) \times v}{w} \quad (2)$$

where C_o (mg L^{-1}) and C_e (mg L^{-1}) represents the initial and equilibrium ammonium concentration, respectively; v (L) is the

aqueous solution volume and w (g) is the mass of zeolite. The ammonium equilibrium sorption was evaluated according to the Langmuir isotherm using Equation (3):

$$qe = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (3)$$

where q_m (mg g^{-1}) is the maximum sorption capacity and K_L (L mg^{-1}) is the Langmuir sorption equilibrium constant.

Ammonium sorption kinetics
The homogeneous diffusion (HPDM) and shell progressive model (SPM) were selected to describe the ammonium extraction kinetics by NZs. In the HDM model zeolite particles are considered as a quasi-homogeneous media and the sorption diffusion rate controlling step on the spherical particles leads to:

(i) If particle diffusion Dp $(m^2 s^{-1})$

controls the sorption rate: $-\ln\left(1 - X(t)^2\right) = \frac{2 \; \pi^2 D_p}{r^2} t \quad (4)$

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(ii) If liquid film diffusion Df $(m^2 s^{-1})$

controls the sorption rate: $-\ln(1 - X(t)) = \dfrac{D_f C}{h\, r\, C_z} t$ (5)

where $X(t)$ is the fractional attainment of sorption equilibrium (q_t/q_e) on the zeolite phase at time t, C_s and C_r (mg kg^{-1}) are the concentrations of solute in solution and in the zeolite, respectively; r is the average radius of zeolite particles (4×10^{-4} m), t is the contact time (s); and h is the thickness of film around the zeolite particle (1×10^{-5} m for poorly stirred solution).

The SPM describes the sorption process by a concentration profile of the solution containing ammonium ions advancing into a spherical particle partially saturated.[37] The removal mechanism involves diffusion of ammonium from the aqueous solution into the zeolite phase through a number of possible resistances. The ammonium species originally in the solution phase must diffuse across the liquid film surrounding the zeolite particle, transfer across the solution particle interface, diffuse into the bulk of the particle and possibly interact with negative charged sites on the zeolite particles. The sorption rate controlling steps on the zeolite particles leads to:

(a) For fluid film diffusion: $X(t) = \dfrac{3 C_{A0} K_F}{a_s C_{So}} t$ (6)

(b) For particle diffusion:

$$\left[1 - 3(1 - X(t))^{\frac{2}{3}} - 2X(t)\right] = \dfrac{6 D_e C_{A0}}{a_s^2 C_{So}} t \quad (7)$$

(c) For chemical reaction: $\left[1 - (1 - X(t))^{1/3}\right] = \dfrac{K_s C_{A0}}{r} t$ (8)

where D_e is the effective diffusion coefficient of ammonium ions in the zeolite phase (m^2 s^{-1}), C_{A0} and C_{So} are the concentration of ammonium in solution and at the zeolite unreacted core, respectively (mg L^{-1}) and a_s is the stoichiometric coefficient. $X(t)$ values could be calculated by using Equation (9):

$$X(t) = \dfrac{q_t}{q_e} \quad (9)$$

Where q_t and q_e are zeolite ammonium loading at time t and when equilibrium is attained (mg g^{-1}), respectively.

All experimental data were treated graphically and compared with all fractional attainment of equilibrium functions ($F(X) = f(t)$) (Equations (4)–(8)).

RESULTS AND DISCUSSION

Zeolite samples characterization

X ray diffraction (XRD) patterns of NZ samples are shown in Fig. 2. Clinoptilolite and mordenite were found to be the major components of NZ1 and NZ2, but small amounts of other crystalline phases like quartz, feldspars and unaltered glass were also detected. In the case of NZ3 in addition to clinoptilolite, mordenite and some small amounts of heulandites, the presence of quartz and feldspars were also detected.

XRF analysis, of the samples as summarized in Table 1 revealed the predominance of SiO$_2$ and Al$_2$O$_3$ and to a lesser extent,

appears when the ratio SiO$_2$/Al$_2$O$_3$ is between 4.3 and 6.5 and the ratio (K$_2$O + Na$_2$O)/ (MgO + CaO) ranges from 1.5 to 0.8.[38] The high overall nSi/nAl > 4 ratio in the samples can be attributed to the existence of significant proportions of feldspars, quartz and unaltered glass.[38] Generally, major chemical components (SiO$_2$ and Al$_2$O$_3$) showed small differences when compared with other natural zeolites from different deposits (Table 1) and this may be due to their different geological formation environment.

It should be mentioned, especially for NZ3, that it has high contents of Fe$_2$O$_3$ (7.8%) and CaO (4.4%) in comparison with NZ1 and NZ2 as well as in comparison with the other natural zeolites, as can be seen in Table 1. The presence of the two minerals can be an added benefit for the zeolite for waste water treatments as they can provide better phosphate removal potential. In the presence of Ca (II), phosphate removal is promoted by the formation of calcium phosphate minerals,[15,40] and in the presence of iron oxides, phosphate sorption is fostered by complexation with <FeOH surface groups.

The acid–base properties were determined using the PZC method. From the analysis of the variation of ΔpH with pH, as can be seen in Fig. S1 (Supporting information), values of 9.1 ± 0.3, 7.9 ± 0.2 and 7.4 ± 0.2 for NZ1, NZ2 and NZ3, respectively, were determined. Values were related to the measured ammonium exchange capacities and results shown that NZ3 with the lowest value shows the highest sorption capacity. Values of the pH of treated ammonium model samples had values of pH covering the range of pH$_{PZC}$. Then under these conditions zeolites with the lowest point of zero charge will provide the highest sorption capacity for cations such as ammonium. Observed fluctuations on ΔpH versus pH data are attributed to the presence of minerals with basic properties such as calcite. These are present in minor quantities and then from sample to sample small variations are expected. Although little PZC data of natural zeolites could be found in the literature, values of 6.5 to 7.5 were reported by Kosmulski,[44] while data for clays, the closest mineral family, showed values from 8.5 up to more acidic values of 5.1.[45] Guaya *et al.*[15,46] reported values of 5.5 for a natural clinoptilolite in the sodium form and 4.5 ± 0.2 when impreganted with hydrated aluminium oxide or 6.4 ± 0.4 when impregnated with hydrated ferric oxide, as described also by Alshamare *et al.*[47] Values of pH$_{PZC}$.

Fe$_2$O$_3$ and CaO, although in sample NZ3 their contribution is as

important as the Al$_2$O$_3$ in NZ1 and NZ2. The formation of zeolite

FESEM images showed a network of crystal clusters for the NZ (supporting information, Fig. S2) with homogeneous crystal size

distribution. The images showed a few smaller particles with spherical shapes and mostly large particles and agglomerates with irregular shapes. The difference in the morphology as evident at the edges is probably due the way the sample was processed (e.g. milling conditions may result in small differences in appearance). It is observed that the clinoptilolite crystal phase has characteristi- cally plate-like morphology (Fig. S2) with large cavities and entries to the channels inside the zeolite framework, and mordenite phase has thinner sheets in accordance with the zeolites morphology.[48]

The FESEM−EDX analysis revealed the presence of O, Na, Mg, Al, Si, K, Ca and Fe as the main elements in the surface composition of the zeolites (Table S1 (supporting information)). Table S1 also reveals the chemical composition of different natural zeolites. Sim- ilar values were obtained for the major elements (O, Al, Si) which are the main building blocks of zeolite structure; but differences were attributed to exchangeable cations (K, Na, Ca) and for the Fe content. As described earlier from the XRF analysis, NZ3 showed a higher content of Fe and Ca but the values were found comparable with those from a study with a zeolite from Yemen (Table S1).

Table 1. Chemical composition (%) (w/w) of raw natural zeolites determined by XRF and data on natural zeolites from the main world deposits in Turkey, Iran, China, Australia, Greece, Chile and Yemen

	NZ1	NZ2	NZ3	Turkish zeolite [31]	Iranian zeolite [32]	Chinese zeolite [39]	Australian zeolite [33]	Chilean zeolite [19]	Greek zeolite [40]	Yemeni NZ [41]
SiO_2	62	68	68	70.9	70.0	66.4	70.4	67.0	68.3	69.9
Al_2O_3	10.2	11.1	9.2	12.4	10.5	12.2	12.9	13.0	13.2	11.8
Fe_2O_3	1.9	2.0	7.8	1.2	0.5	1.0	1.4	2.0	1.4	2.4
CaO	3.9	2.4	4.4	2.5	0.2	3.2	3.3	3.2	0.8	2.4
MgO	0.5	0.8	0.5	0.8	-	1.0	1.1	0.7	1.2	0.2
K_2O	1.1	1.1	0.5	4.5	4.9	1.4	1.6	0.5	1.7	3.7
Na_2O	0.3	0.4	0.3	0.3	2.9	0.7	1.2	2.6	4.1	1.1

Table 2. Influence of pH on the ammonium sorption capacity for solutions having an initial concentration of 864 mgN-NH$_4$ L^{-1} and a phase ratio of 0.2 g NZ in 25 mL of aqueous solution

	q_e (mgN-NH$_4$ g^{-1})		
	pH = 7.6 ± 0.1	pH = 8.0 ± 0.2	pH = 9.0 ± 0.1
NZ1 (pH$_{PZC}$ 9.1 ± 0.3)	19.4 ± 0.6	23.4 ± 0.8	15.7 ± 0.9
NZ2 (pH$_{PZC}$ 7.9 ± 0.2)	23.9 ± 0.8	27.4 ± 0.9	26.7 ± 1.2
NZ3 (pH$_{PZC}$ 7.4 ± 0.2)	35.1 ± 1.1	39.6 ± 1.2	32.7 ± 1.2

Table 3. Isotherm parameters for ammonium sorption by natural zeolites NZ1, NZ2 and NZ3 for a phase ratio of 0.2 g NZ and 25 mL of aqueous solution and constant temperature of 22 ± 1 °C

|	Langmuir			Freundich		
	q_m	K_L	R^2	K_F	n	R^2
NZ1	27.4 ± 2	0.0007	0.98	0.063	1.2	0.92
NZ2	32.2 ± 2	0.001	0.98	0.31	1.7	0.92
NZ3	51.8 ± 4	0.0036	0.99	0.68	1.6	0.95

Ammonium sorption capacity: pH dependence and equilibrium isotherms

Although the removal of ammonium is mainly driven by an ion exchange process, the acid–base properties of both ammonium and the zeolite surface can be determined by identifying the optimum pH of the aqueous medium; thus the dependence on aqueous pH is an important factor controlling ammonium sorption.[49] Then sorption capacities of the NZ samples were determined in the expected pH values of treated urban waste waters ranging from 7 to 9 and the results are summarized in Table 2. Ammonium sorption capacities of each zeolite reached the highest values at pH 8 and then, as is expected from its acid–base properties, started to decrease with further increase in pH as it is transformed to a non-protonated form (NH$_3$).The q_e -pH functions showed constant values between pH 4 to 9 as described previously by Guaya et al.,[15,43] Alshameri et al.[41] and Moussavi et al.[49] The highest sorption values of three zeolite samples were attained at pH values approaching the PZC. In comparison, it was found that the maximum sorption values of the three zeolites ranged from 33 to 40 mgN–NH$_4$ g^{-1} and such differences could be associated with the different composition of the exchangeable ions on the zeolites (K, Na, Mg, and Ca). For waste streams with pH values below 6, while from the chemical speciation point of view ammonium will be the dominant species for inorganic ammonium forms from the acid–base properties of the zeolite structure the exchange sites will be partially dissociated. However, results in Table 3 show that the weight of the chemical speciation in solution plays a dominant role in the ion-exchange reaction.

Analysis of the sorption capacity in aqueous phase (data not reported) confirms the release of Na$^+$ and, in minor degree, of K$^+$, Mg^{2+} and Ca^{2+}. EDAX data revealed also the reduction in content of these cations in the ammonium loaded zeolites.

Thus, the sorption of ammonium by the natural zeolites could be

(i) Ion exchange reaction with M$^+$ from the zeolite sites as it is described by Equation (10):

$$Z^-M^+ + NH_4^+ \longrightarrow M^+ + Z\text{-}NH_4^+ \qquad (10)$$
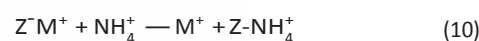
described by the combination of two main processes:[50]

where M represent any exchangeable cation present on the NZ (Na, K, Ca, Mg) and Z$^-$ represents the ionogenic groups of the zeolite structure.

(ii) Acid–base dissociation reaction of ammonium ions

as it is described by Equation (11):

$$NH^+ \leftrightarrow H^+ + NH_3 \qquad \log K_a = -9.3 \qquad (11)$$
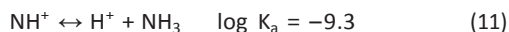
According to Equation (11), NH_4^+/ NH_3 equilibrium in solution is pH dependent and thus only the ionized form can be removed from solution by ion exchange. At pH 8 and below total ammo- nium is substantially present in the ionized form, therefore, it is rea- sonable to assume that these conditions would favor the removal process.

Equilibrium sorption isotherms with ammonium solutions cover- ing the ammonia concentration range expected in effluents from the high rate activated sludge stage (25 to 100 mgNH$_4^+$ L^{-1}) and inside streams of sludge anaerobic digestion (400 to 1600 mgNH$_4^+$ L^{-1}) are shown in Fig. 3. The ammonium sorption data are well described by the Langmuir isotherm ($R^2 \geq 0.98$) while Freundlich isotherm ($R^2 \leq 0.95$) (Table 3 and Fig. 3) provides a good descrip- tion only at the lower concentration ranges. Therefore, monolayer and homogenous sorption or/and ion exchange at specific and equal affinity sites available on the zeolites surface is supposed to occur. A favorable sorption is revealed by the values of K_L (from 0.0007 to 0.0036).[28] The maximum sorption capacities was found to be 27.4 ± 2 mg-N g^{-1}, 32.2 ± 2 mg-N g^{-1} and 51.8 ± 4 mg-N g^{-1} for NZ1, NZ2 and NZ3, respectively.

XRD patterns of the NZs after sorption (Fig. S3) showed that the differences could be observed only in the intensity of reflexions, but no changes were observed with respect to their position.
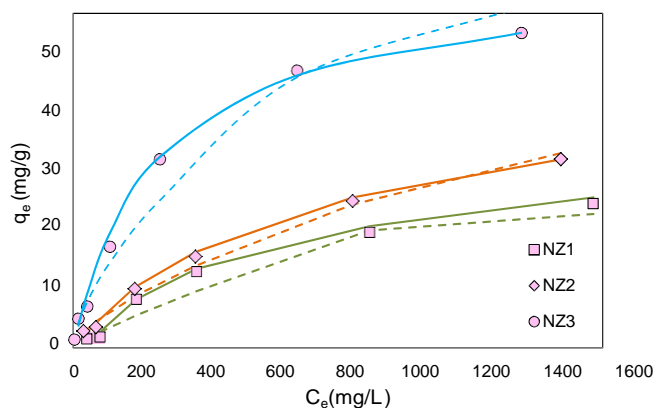
Figure 3. Experimental and theoretical equilibrium isotherms for ammonium removal by natural zeolites NZ1, NZ2 and NZ3 for a phase ratio of 0.2 g NZ and 25 mL of aqueous solution at room temperature $22° \pm 1$. (Dots: experimental data, line: the Langmuir predicted values, dashed line: the Freundlich predicted values.)

Table 4. Desorption efficiency of ammonium loaded NZs using NaOH, NaCl and mixtures NaOH/NaCl with aqueous solutions to zeolite ratios of 25 mL per 1.2 g at room temperature 22 °C

	NZ1 EX(%)	NZ2 EX(%)	NZ3 EX(%)
0.02 mol L^{-1} NaOH	94 ± 3	97 ± 3	88 ± 2
0.1 mol L^{-1} NaCl	89 ± 4	96 ± 2	89 ± 4
0.02 mol L^{-1} NaOH/0,1 mol L^{-1} NaCl	97 ± 2	98 ± 1	92 ± 5

Samples were dried at low temperature to avoid losses of soluble forms of ammonium as NH_3 (g). Similar results were found by Alshameri *et al.*[41] and Guaya *et al.*[15]
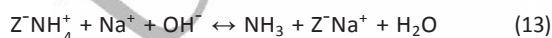
Zeolites reusability: ammonium desorption

Results from desorption efficiency studies of ammonium from loaded zeolites using NaOH, NaCl and mixtures NaOH/NaCl are summarized in Table 4. Desorption was found to be a fast process (data not shown) and equilibrium was achieved in less than 20 min. The regeneration tests showed that no significant loss of zeolite capacity was observed after five consecutive cycles. The rationale desorption process is that the reverse of the exchange reaction (Equation (11)) and the conversion of ammonium to ammonia could be possible by increasing the pH as it is described by reactions (12) and (13):

(i) Ion exchange reaction with sodium ions from NaCl:

$$Z^-NH_4^+ + Na^+ \leftrightarrow NH_4^+ + Z\text{-}Na^+ \qquad (12)$$
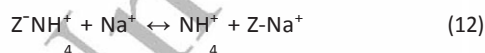
(ii) Ammonium conversion to NH_3 n basic media NaOH (pH > 12):

$$Z^-NH_4^+ + Na^+ + OH^- \leftrightarrow NH_3 + Z^-Na^+ + H_2O \qquad (13)$$

Sodium rich solutions of NaCl and NaOH and a mixture of NaCl/NaOH provided high desorption ratios with values above 90%, for NZ1 and NZ2 samples and only recovery ratios between 85 and 95% were measured with NZ3. The use of sodium base brines as a means to regenerate NaCl is based on the selectivity order of natural zeolite among cations as reported by Sarioglu[25] with the following sequence
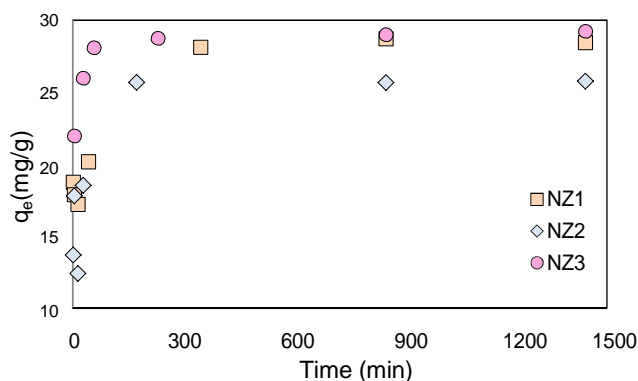

Figure 4. Influence of contact time on NH_4^+ removal sorption capacity of natural zeolites NZ1 (q_m 19.4 ± 0.6), NZ2 (q_m 23.9 ± 0.8), and NZ3 (q_m 35.1 ± 1.1), for a solid−liquid ratio 0.2 g of zeolite and volume of 25 mL for an initial concentration of 864 mgNH4 L^{-1} and a pH of 7.7 ± 0.3.

Ammonium sorption kinetics of powder zeolites in stirred reactors

Ammonium sorption kinetic data (Q_t versus time) for NZ zeolites are shown in Fig. 4. The ammonium sorption rates are comparable with other natural and synthetic zeolites demonstrating a very fast sorption step where more than 60% of the equilibrium attainment ($X(t) = 0.60$) is reached in less than 10 min followed by a slower sorption step controlled by a typical particle diffusion profile as encountered in most of the polymeric ion-exchange resins.[37,51] Sorption profiles for the three zeolites show the typical behavior of a sorption material where the solid surface plays an important role. Ion-exchange sites are distributed along the microporous structure and then diffusion processes are the rate determining step.

Comparing zeolites samples NZ1 and NZ2 need high times to reach equilibrium (60 min for Xt >0.95), while for NZ3 only 30 min were needed to reach Xt >0.95. Analysis of the fractional equilibrium attainment functions (F(X) = f(t)) by using both HDM and SPM models indicated that sorption rate control of ammonium ions is particle diffusion. A first stage of NH_4^+ diffusion from the solution to the external surface of zeolite is followed by a sorption stage along the zeolite internal surface. The linear regression analyses of the rate control equations are summarized in Table 5. The linear regression coefficients (R^2) values are closer to 1 for the equations considering particle diffusion as rate determining step. Both models (HPDM and SPM) provided a good description of the experimental data as can be seen in supporting information (Fig. S4). Particle diffusion coefficients calculated ranged from 1.2 to 5.1×10^{-12} m^2 s^{-1}. These values are consistent with the results reported for ammonium sorption on natural clinoptilolite at low initial ammonium concentrations and with diffusion coefficients determined on the removal of heavy metals by natural zeolites.[39]

$$K^+ > NH_4^+ > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}.$$

ts for ammonium recovery from waste water treatment plants incorporating high rate activated sludge stages: process integration

Three ammonium containing effluents from urban WWTPs were evaluated: (a) secondary from a conventional activated sludge reactor, with values of ammonium in the order of 15 to 20 mg L^{-1}; (b) effluent of high rate activated sludge or an A-stage reactor with values of ammonium up to 50 – 100 mg L^{-1}; and (c) side streams generated in the sludge anaerobic reactor with concentrations of ammonia between 400 and 1600 mgNH$_4$ L^{-1}. The applicability of

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that have direct implications for the removal of phosphate

Table 5. Results of the kinetic data analysis for ammonium sorption by powder natural Yemeni zeolites (NZ1, NZ2, NZ3) in stirred tanks using both HPDM and SPM models

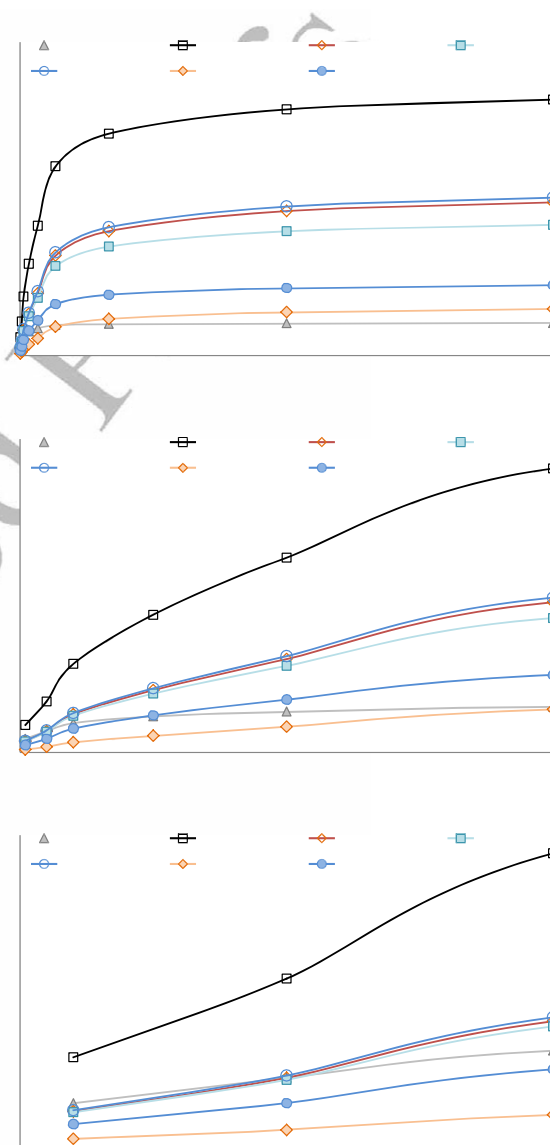|	HPDM				SPM					
	$\ln(1 \ X^2)$		$\ln(1 \ X)$		X		$[3 \ 3(1 \ X)^{2/3} \ 2X]$		$[1 \ (1 \ X)^{1/3}]$	
	R^2	D_f (m^2 s^1)	R^2	D_p (m^2 s^1)	R^2	K_F (m s^1)	R^2	D_p (m^2 s^1)	R^2	k_s (m s^1)
NZ1	0.99	$1.24 \ 10^{-12}$	0.79	$1.18 \ 10^{-10}$	0.71	$2.4 \ 10^{-11}$	0.98	$4.0 \ 10^{-12}$	0.93	$2.6 \ 10^{-13}$
NZ2	0.96	$2.1 \ 10^{-12}$	0.86	$5.8 \ 10^{-10}$	0.73	$3.7 \ 10^{-11}$	0.96	$3.0 \ 10^{-12}$	0.82	$2.2 \ 10^{-13}$
NZ3	0.93	$5.1 \ 10^{-12}$	0.91	$5.4 \ 10^{-10}$	0.64	$4.1 \ 10^{-11}$	0.92	$6.0 \ 10^{-12}$	0.84	$2.8 \ 10^{-13}$

the evaluated Yemeni zeolite samples was evaluated in terms of removal capacity and the treated effluent residual values achieved under these conditions were further compared with published data for natural zeolites. Table S2 summarizes both ammonium sorption and desorption equilibrium parameters.

By using the Langmuir or Freundlich isotherms theoretical pre-dictions plotted for comparison are shown in Fig. 5 for effluents with high concentration of ammonium (from 100 to 1600 mgNH$_4$ L^{-1}), effluents with medium ammonium concentrations (from 10 to 100 mgNH$_4$ L^{-1}) and effluents with low ammonium concentra-tions (from 1 to 10 mgNH$_4$ L^{-1}). It should be mentioned that in most cases (Table S2) the pH used in the experimental studies was not reported and in most cases the sorption isotherms were not car-ried out at constant pH values. Experiments conducted with NZ1, NZ2 and NZ3 were carried out at pH 8.

Comparison of isotherms in the three ranges of ammonium con-centration indicates that the sorption capacity evaluated for NZ3 was up to two times higher than those reported for the other nat-ural zeolites. In addition, the sorption capacity of NZ1 sample was similar to the highest values reported for the different zeolites eval-uated. The better performance of NZ3 sample could be associated with the higher content of clinoptinolite and mordenite and also the presence of heulandites. The sample is also characterized by the presence of higher content of iron oxide.

The capacity to reduce the ammonium concentration to the tar-get values as defined by most of the Environmental Regulation agencies (e.g. 15 mg NH$_4$ L^{-1} for treated water to be discharged to water bodies or 1 mgNH$_4$ L^{-1} according to coming regulations) as a function of the zeolite dose is shown in Fig. 6. The ammonium residual values decreased with the increase of the dose. For zeo-lites NZ1 and NZ2, a reduction of the concentration respectively from 77 to 3 mgNH$_4$ L^{-1} and from 91 to 4.3 mgNH$_4$ L^{-1} was achieved for zeolite doses of 40 gNZ L^{-1}. However, for NZ3, which showed a high sorption capacity at higher ammonium concentrations (see Fig. 3 and Table 3), under the low concentration range demon-strated higher ammonium residual concentrations (14 mg L^{-1} for a 40 gNZ L^{-1} dose). Thus, the NZ tested demonstrated sufficient effi-ciency to remove ammonium up to the 15 mg L^{-1} threshold in the final effluent. But if the target value to achieve in the final effluent is 1 mg L^{-1}, then it invariably dictates the need for an increase of the zeolite dosage.

A distinctive behaviour of NZ3 on reaching permissible levels for ammonium in comparison with NZ1 and NZ2 has been observed although having slightly higher ammonium sorption capacity. These differences could be associated with the effect of other cations present in the waste water (Na, Ca, Mg, K) influencing the sorption capacity in comparison with the model solutions. It must be noted that NZ3 has a higher content of Ca and Fe oxides
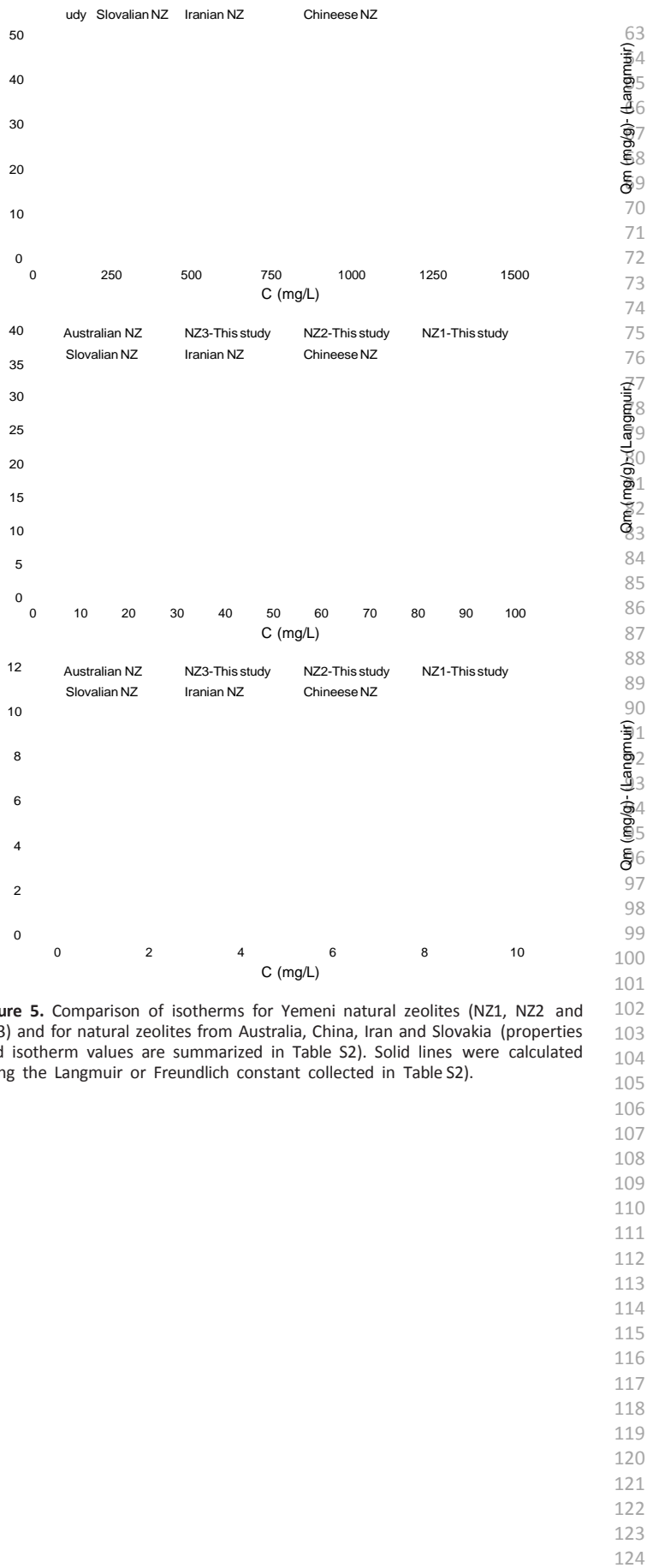

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30
20
10
0

udy   Slovalian NZ   Iranian NZ   Chineese NZ

0   250   500   750   1000   1250   1500

C (mg/L)

Q_m (mg/g) - (Langmuir)

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Australian NZ   NZ3-This study   NZ2-This study   NZ1-This study
Slovalian NZ   Iranian NZ   Chineese NZ

0   10   20   30   40   50   60   70   80   90   100

C (mg/L)

Q_m (mg/g) - (Langmuir)

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90

12

10

8

6

4

2

0

Australian NZ   NZ3-This study   NZ2-This study   NZ1-This study
Slovalian NZ   Iranian NZ   Chineese NZ

0   2   4   6   8   10

C (mg/L)

Q_m (mg/g) - (Langmuir)

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Color Figure - Online only

Figure 5. Comparison of isotherms for Yemeni natural zeolites (NZ1, NZ2 and NZ3) and for natural zeolites from Australia, China, Iran and Slovakia (properties and isotherm values are summarized in Table S2). Solid lines were calculated using the Langmuir or Freundlich constant collected in Table S2).
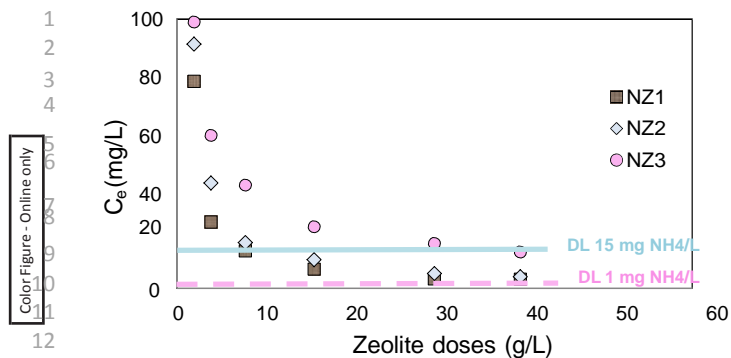
Figure 6. Variation of the residual ammonium concentration (C_e (mg L^{-1})) in solution as a function of the zeolite doses (gZ L^{-1}). Solid lines described the discharge limits defined by the EC1991 on treated waste water limits for ammonium and solid line describe the expected new regulations. Volume of aqueous solution was 25 mL and the initial ammonium concentration was 864 mgN-NH$_4$ L^{-1} and a pH of 7.6 ± 0.2 (DL: discharge limit).

(present in waste water) via complexation with <FeOH groups or formation of Ca-phosphates. Values of phosphate removal were not included in the scope of the work but the removal efficiency of NZ3 was reported to be higher than that of NZ1 and NZ2, and it may be postulated that this co-removal mechanism affected the ammonium removal.

CONCLUSION

The mineralogical characterization of three natural zeolites (NZ1, NZ2, NZ3) collected from different regions of Yemen indicated that clinoptilolite and mordenite were the major components of NZ1 and NZ2, but small amounts of other crystalline phases like quartz, feldspars and unaltered glass were also detected. For NZ3, in addition to clinoptilolite, mordénite some small amounts of heulandite, quartz and feldspar was also detected.

The three zeolite samples provided high ammonium sorption capacities for concentrated ammonium streams of 27 to 51 mgNH$_4$ g^{-1} at pH values of 8.0 ± 0.2. Sample NZ3, with the highest CaO(s) and Fe$_2$O$_3$(s) contents showed the highest sorption capacities among the three studied zeolites; and its maximum sorption capacity was also recorded to be higher than those reported for other natural zeolites in the literature. Loaded zeolites were efficiently regenerated using NaOH and NaOH/NaCl brines (0.1 mol L^{-1}). Recovery of ammonia from regeneration solutions, by using for example air-striping or liquid–liquid contactors will provide the possibility of reusing the stripping solutions for several cycles. The number of cycles will depend on the accumulation of cations as Ca(II) and Mg(II) or dissolved organic matter.

The ammonium sorption kinetics of the powdered zeolite samples was controlled by particle diffusion and was well described by the HPDM and SPM models. Faster kinetics was exhibited by NZ3 in comparison with those of the two other studied zeolites. Comparison of the kinetic data for the characterized Yemeni zeolite samples with published results for other natural and synthetic zeolites demonstrate their higher performance, which could be used in stirred tank applications. Doses of 40 gNZ L^{-1} was found to be suitable to achieve ammonium residual levels below 1 mgNH$_4$ L^{-1} from diluted ammonium streams generated in high rate activated sludge stages and below 10 mgNH$_4$ L^{-1} from concentrated ammonium streams generated in side streams of anaerobic digestion of sewage sludge.

Supporting Information

Supporting information may be found in the online version of this article.

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