Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors

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HIGHLIGHTS

- A natural zeolite was evaluated to recover ammonium in column experiments.
- Loaded zeolite was regenerated and rich concentrates were used in a LLMC system.
- Hollow fibre liquid-liquid membrane contactors were used to produce liquid fertilizers.
- The closed-loop configuration allowed recovery ratios of ammonia higher that 98%.
- Concentrated solutions reached up to 2–5% wt. of N.

GRAPHICAL ABSTRACT
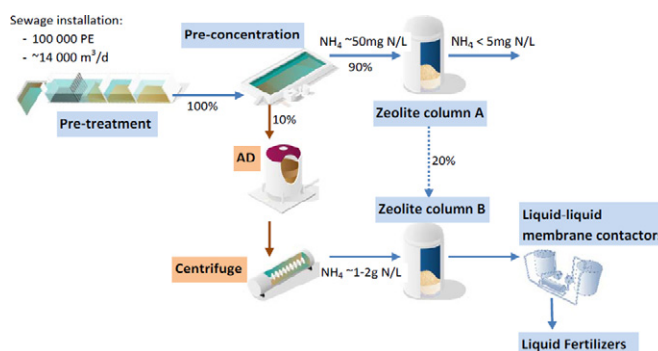
ARTICLE INFO

ABSTRACT

The integration of up-concentration processes to increase the efficiency of primary sedimentation, as a solution to achieve energy neutral wastewater treatment plants, requires further post-treatment due to the missing ammonium removal stage. This study evaluated the use of zeolites as a post-treatment step, an alternative to the biological removal process. A natural granular clinoptilolite zeolite was evaluated as a sorbent media to remove low levels (up to 100 mg-N/L) of ammonium from treated wastewater using batch and fixed bed columns. After being activated to the Na-form (Z-Na), the granular zeolite shown an ammonium exchange capacity of 29 ± 0.8 mg N-NH$_4^+$/g in single ammonium solutions and 23 ± 0.8 mg N-NH$_4^+$/g in treated wastewater simulating up-concentration effluent at pH = 8. The equilibrium removal data were well described by the Langmuir isotherm. The ammonium adsorption into zeolites is a very fast process when compared with polymeric materials (zeolite particle diffusion coefficient around 3×10^{-12} m^2/s). Column experiments with solutions containing 100 mg N-NH$_4^+$/L provide effective sorption and elution rates with concentration factors between 20 and 30 in consecutive operation cycles. The loaded zeolite was regenerated using 2 g NaOH/L solution and the rich ammonium/ammonia concentrates 2–3 g/L in NaOH were used in a liquid-liquid membrane contactor system in a closed-loop configuration with nitric and phosphoric acid as stripping solutions. The ammonia recovery ratio exceeded 98%. Ammonia nitrate and di-ammonium phosphate concentrated solutions reached up to 2–5% wt. of N.

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1. Introduction

The most common technology used in urban wastewater treatment is based on the conventional activated sludge (CAS) process, which uses large amounts of energy for aeration and loses the potential energy content of the organic load. Recently, it has been estimated that wastewaters contains more chemical energy (as organic pollution load) than is needed for its treatment using CAS. However, the low organic content (1 to 2 g/L) is the main barrier to overcome in order to use this energy. Indeed, the energy balance of centralized sewage treatment can be improved by up-concentrating sewage to achieve energy positive wastewater treatment plants, thus different pre-concentration steps have been proposed (Verstraete et al., 2009; Jenicek et al., 2013; Meerburg et al., 2015). In the implementation of up-concentration techniques (e.g., bio-flocculation) a high-load organic stream is generated thus promoting the bio-methane production enhancement (Meerburg et al., 2015). This solution increases the efficiency of primary sedimentation, eliminating the chemical coagulant demand by recirculation of sewage sludge to the primary settler. However its implementation as a mainstream sewage treatment process requires further post-treatment, due to the missing ammonium removal approach and the relatively lower effluent quality. Most of the post-treatment solutions for the novel up-concentration processes are focused on autotrophic nitrogen removal (Lotti et al., 2015; Wett et al., 2015) or on membrane processes to ensure effluent discharged standards (Diamantis et al., 2014), thus, the possibility to introduce ammonium recovery solutions is a recently postulated alternative that needs further development (Galí et al., 2014).

Nitrogen is an essential nutrient for all living forms, however, an excessive growth of algae and the consequently depletion of the dissolved oxygen is an effect of the nutrient overloading in surface water receiving bodies (Blaas and Kroeze, 2016). Therefore, the removal of ammonium from wastewater to avoid the consequences of eutrophication processes has now become a challenge. In order to reach the required low levels of N-NH$_4^+$ in the discharged effluents, which can be as low as 1 mg NH$_4^+$/L (Salomon et al., 2016), a nitrogen treatment step is essential as part of the wastewater treatment process. Moreover, nitrogen is a key component for fertilizer production and indeed, it is critical to agricultural uses.

Nitrogen removal is commonly achieved by means of a biological nitrification–denitrification process, where ammonium is transformed to nitrogen gas (Zhang et al., 2011). In addition to incoming wastewaters, recycled streams within the WWTPs may also contribute to the nitrogen load applied to the biological nitrogen removal process. Side streams arising from dewatering of digested sludge (typically 500–1000 mgNH$_4^+$/L) are recirculated to the water line, increasing the nitrogen loading on the WWTPs (Wirthensohn et al., 2009). Although representing only a small fraction of the overall flow-rate (<2%), the high concentration of side streams could contribute up to 25% of the total nitrogen load. Anaerobic ammonium oxidation (Anammox) appears as a promising alternative to the conventional process due to the low energy consumption and the suppression of the necessity of an external carbon source (typically methanol) to denitrify (Ali and Okabe, 2015; Ma et al., 2016). However, the Anammox technology still present relevant limitations such as long start-up periods, strong sensitivity to operation conditions variation and a high susceptibility to reactor threats (Jin et al., 2012; Tian et al., 2015). Additionally, it is expected that in the future these biological processes may not be able to sustain the nitrogen removal ratios required to meet the regulated discharge values. Moreover, ammonium is at present increasingly considered a resource, and not only a compound that has to be removed from wastewater (Batstone et al., 2015). Consequently, there has been a renewed interest to recover nutrients from waste streams as a synergy of economic, energy and environmental considerations (Sareer et al., 2016).

Physicochemical methods have been widely used for the removal and recovery of ammonium species from waste streams in a usable form to supplement existing ammonia production. Inorganic cation exchange materials, such as zeolites are suitable for the selective removal of ammonium. Zeolites provide a framework structure with micro- and meso-pores (Hedström, 2001) with better performance than polymeric ion-exchange resins due their higher selectivity to ammonium ions in the presence of common competing cations (e.g., sodium, potassium, calcium and magnesium) (Bashir et al., 2010). Both, natural and synthetic zeolites have been widely evaluated for ammonium removal due to its high cation exchange capacity (Thornton et al., 2007a) and they have been identified as suitable sorbents for wastewaters taking benefit of their properties (e.g., mechanical and thermal, cation-exchange capacity, easy operation and maintenance, low treatment costs, high selectivity and the release of non-toxic exchangeable cations (K$^+$, Na$^+$, Ca^{2+} and Mg^{2+}) (Millar et al., 2016; Thornton et al., 2007b; Jorgensen and Weatherley, 2003).

Regeneration of loaded ammonium zeolites generates rich ammonium/ammonia concentrates (2–6 g NH$_3$/L) in NaCl, NaOH or NaOH/NaCl solutions. As the ion exchange concentration step involves pre-treatment for particulate matter removal by sand filters or membrane ultra-filtration, the ammonia concentrates quality is suitable for the integration of hollow fibre liquid-liquid membrane contactors (HFMCs) (Lauterböck et al., 2013) as separation and concentration step.

This process has been used as a polishing step to remove low levels of ammonia/ammonium from industrial effluents (up to 200 mgNH$_4^+$/L) (Hedström, 2001; Klaassen et al., 2008; Mandowara and Bhattacharya, 2011; Tan et al., 2006). HFMCs using polyvinylidene fluoride (PVDF) and polypropylene (PP) have shown high ammonia removal efficiencies dependent on the feed pH and independent on the feed ammonia concentration using strong acids as stripping phase (e.g., sulfuric and hydrochloric acids) (Ashrafizadeh and Khorasani, 2010). Compared to conventional scrubbers, liquid-liquid membrane contactors have a much larger specific surface area, thus foot-print and capital costs are reduced (Licon et al., 2014; Mandowara and Bhattacharya, 2011). The aim of this study is to evaluate the integration of a natural zeolite for the selective extraction of ammonium from treated wastewater simulating up-concentration effluents and the subsequent ammonium concentration and purification step using hollow fibre membrane contactors by producing NH$_4$NO$_3$ and (NH$_4$)$_2$(HPO$_4$) for potential use as a liquid fertilizer.

2. Materials and methods

2.1. Modification of natural clinoptilolite (Z) zeolite to sodium form (Z-Na)

A natural zeolite (Z) from Slovakian Republic (Zeocem Co) was used. Zeolites particles below 200 μm were used for batch experiments and 800–1200 μm particles were used for column experiments. A dried zeolite sample (30 g) was treated with 250 mL of NaCl (6 g/L) under reflux conditions for 4 h in two consecutive cycles to obtain the sodium form (Z-Na).

2.2. Equilibrium and kinetic evaluation of ammonium removal by using batch experiments

Ammonium sorption equilibrium: Z-Na samples (0.2 g) were equilibrated with 15 mL of solutions containing 25 mgN-NH$_4^+$/L (with pH ranging from 2 to 11). Experiments were replicated with a treated effluent from the Sant Feliu WWTP (Barcelona – Spain) at pH of 7.7. The average composition of the treated wastewater samples used is shown in Table 1.

Ammonium sorption kinetics: 10 g of Z-Na were equilibrated in 1 L of the Sant Feliu WWTP treated effluent (Table 1) at pH 7.7 ± 0.4. Experiments were performed at room temperature (22 ± 1 °C). Samples were collected at given times to quantify the ammonium concentration. Assays were performed in triplicate and reported data are average values.