**Removal and recovery of ammonium from municipal wastewater by adsorption/ion exchange on an innovative potassium based geopolymer adsorbent**

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**1.Introduction**

Nowadays, 50% of food production relies on ammonia fertilizers. The industrial Haber-Bosch process is used to satisfy the rising demand for fertilizer, but it is very energy-intensive: it consumes 1% of the annual global energy supply, and produces about 1,4% of global CO2 emissions [1]. On the other hand, wastewater (WW) is increasingly considered as a source of water, energy, and plant fertilizing nutrients such as nitrogen and phosphorous [2].

The adsorption/ion exchange process has proven to be a simple, cost-effective, and an environmentally friendly technique and an efficient way to remove and recover ammonium from wastewaters for further industrial uses, such as fertilizer production [3] [4]. Adsorption and ion exchange consist of mass transport between a liquid phase (adsorbate) and a solid phase (adsorbent). The adsorbent should have a particular affinity for the specific adsorbate relative to other substances in the solution [3] and the adsorption capacity and the selectivity of the sorbent materials may vary considerably. Many studies were carried out, but almost all are small-scale laboratory scale tests on natural and synthetic zeolites. However, there is still need for better materials that can achieve high adsorption capacities coupled with good mechanical properties suitable for the application in an adsorption bed. Geopolymers are innovative adsorbent materials that are gaining growing attention because of their excellent mechanical properties and the possibility of designing and fine tuning their adsorption properties. Geopolymers are inorganic polymers that resemble zeolites in many ways: they represent amorphous aluminosilicate materials with a three-dimensional anionic network of AlO4 and SiO4 tetrahedra in which the valence difference of Al(III) and Si(IV) results in a net negative charge, which is balanced by exchangeable cations. The main advantages of geopolymers compared to zeolites are: i) the milder synthesis conditions, ii) simpler preparation, and more importantly iii) the possibility of designing the Al/Si ratio in order to improve the adsorption capacity. The porous structure of geopolymers provides more binding sites, increases permeability, improves mass transfer, and reduces pressure drop. Franchin et al. [5] demonstrated that NH4+ adsorption capacity of metakaolin-based geopolymers was 46% higher than that of natural zeolite and could be efficiently regenerated by NaCl/NaOH.

In this work, a potassium based geopolymer (referred as G13 [6]) synthesized by the Institute of Science and Technology for Ceramics of the National Research Council of Italy (CNR-ISTEC) was used to study the removal and recovery of NH4+ from the effluent of a pilot-scale anaerobic membrane bioreactor (AnMBR), placed in side-stream configuration after an Up-flow Anaerobic Sludge Blanket reactor that treats the partly saline municipal wastewater (MWW) of Falconara Marittima (Italy). In particular, the research focused on: i) the assessment of the operative capacity and selectivity of the material in batch and continuous flow tests with an actual MWW, ii) the optimization of process parameters in order to maximise adsorption and desorption efficiency.

**2. Methods**

The performance of the material in term of N adsorption has been estimated by adsorption isotherm tests, and continuous flow adsorption/desorption breakthrough tests, in a fixed-bed column packed with geopolymer G13. Cations analyses were performed with an HPIC method. All the procedures and methods followed are extensively described by Frascari et al [7]. The continuous tests were performed in a complete automatized pilot plant, consisting in an adsorption/ion exchange PVC column (1.2 m length, 0.21 m of diameter) packed with the adsorbent material for a height of 0.60 m, several LLDPE tanks (0.05-0.15 m3) used to stock the solutions, 1 volumetric pump (flow rate that can be controlled in the 0.25 - 25 L/h range), 3 sensors to monitor temperature, pressure and liquid levels, a datalogger to collect all the data and store them via PC, electrically operated valves to switch the flow in the plant during the adsorption, desorption, washing phases and 1 automatic sampler.

**3. Results and discussion**

*3.1 Adsorption Isotherm*

Two sets of isotherm tests were performed to investigate the performance of the G13: a preliminary 2-point isotherm test conducted with a synthetic NH4Cl solution – to study the maximum operating capacity in absence of competition by other cations – and a complete isotherm with the Falconara MWW effluent. The complete isotherm was repeated after the adsorption/desorption breakthrough test (BT) in a continuous flow apparatus in order to evaluate potential changes in the performances of the geopolymer. The results of the isotherm tests are shown in Figures 1 in terms of NH4+ sorbed concentration versus NH4+ the residual equilibrium concentration in the liquid.

**Figure 1** - Comparison of adsorption isotherms of Geopolymer G13 with (1) NH4Cl synthetic solution, (2) UNIVPM MWW performed before the first breakthrough and (3) after seven cycles.

There are only small differences between the experimental points taken with the NH4Cl synthetic solution (green triangles) and the ones taken with the real MWW (blue squares), suggesting that geopolymer G13 has a good selectivity towards NH4+, in particular when compared to Na+. The latter is, indeed, the most abundant cation normally present in a MWW, it is also detrimental to agricultural purposes, and its presence must be as little as possible in a fertilizer. The isotherm points obtained from the isotherm performed after 7 breakthrough tests (BT) (red points) are consistent with those obtained with the fresh material (blue points). The experimental data were interpolated with the Langmuir and Freundlich models, with the former resulting in the best fitting, with an R2 of 0.93.

*3.2 Continuous flow adsorption/desorption breakthrough tests*

The adsorption/desorption breakthrough tests were conducted in a packed-bed column fed with the Falconara MWW effluent at 24-25°C. The desorption/regeneration procedure was performed eluting the desorbing solution to regenerate the resin and recover the N rich product. The results obtained with Geopolymer G13 in the first BT (BT1) are shown in Figure 2 (adsorption phase) and 3 (desorption phase).

The results showed that the G13 geopolymer has a very good selectivity toward ammonium which is by far the last cation eluted. Ca2+ is the cation with the second-best affinity for the sorbent and, above all the affinity for Na+ is very low (the first cation eluted). The breakpoint for NH4+ at the breakpoint BP (set at 4 mgN/L in the outlet concentration for a municipal effluent) occurs at 149 bed volumes (BVs), meaning that large amount of MWW can be treated before a regeneration step is needed. The NH4+ adsorption yield (Yads, NH4+) calculated at the breakpoint is 0.96, while the operating capacity (ƞNH4+) is 8.42 mgN/gdry resin.

Figure 3 shows that there is a good separation between the desorption of NH4+ and Na+ and Ca2+, allowing the possibility of recovery NH4+ as a pure solution.

**Figure 2**. BT1 N adsorption continuous flow test conducted with Geopolymer G13. Breakthrough curves of ammonium and the competing cations obtained with N-spiked UNIVPM MWW effluent.

*3.3 Optimization of process operational parameters*

The next tests were dedicated to optimize the process by changing and testing various parameters, namely, the empty bed contact time (EBCT) of the adsorption step, the EBCT of the desorption step and the type and concentration of the desorbing solution.

*Effect of different EBCTs on Adsorption*: the effect of EBCT on the removal of N from WWTP has been studied by running three different adsorption breakthrough tests at different values; 10, 7.5 and 5 minutes. The remaining parameters have been kept unvaried. The EBCT reduction decreases the time of the BP, and so the BVs of WW treated. Indeed, the BP occurs at 149 BVs with an EBCT of 10 min, but it decreases to 135 BVs at 7.5 min, reaching a minimum of 124 BVs at 5 min. Operating capacity also follows this trend: it starts with a value of 8.42 mgN/gdry resin for the curve with the higher EBCT, and it decreases to 6.45 and 5.28 mgN/gdry resin for 7.5 and 5 min of EBCT, respectively. These values show that it is possible to reduce the EBCT to 7.5 min and increase the productivity of the plant with an almost negligible drop in performance, but the further reduction of the EBCT to 5 min caused a further and significant reduction in performances.

*Desorption optimization*: the effect of the EBCT in the desorption phase was preliminarily studied, varying it between 120, 60 and 20 minutes, with KCl 1% as desorbing solution. No drop in the performances was registered, so an EBCT of 20 minute was chosen to run all the following tests. The optimization of the desorption phase was mainly meant to test the feasibility of a fractionate desorption with the scope of separating Na+ desorption from N and obtain two fractions: the first rich in Na+ to be disposal, the second rich in ammonium to be reused in N fertilizer production. In a first step, KNO3 has been tested as desorbing solution instead of KCl to avoid the presence of chloride in the desorbed product. Then the concentration of KNO3 was increased from 1.3% to 6.7% in order to obtain a faster desorption and a more concentrated desorbed product. Since while desorbing with a 1% KCl about all the Na+ eluted within the first 5 BVs, while N was almost retained, an optimization was performed to try a “fractionated desorption”: KCl 1% was used as the desorbing solution for the first 5 BVs, then it was switched with KNO3 6.7%. The results showed (Figure 3) that the fractionated desorption is feasible also at higher regenerant concentration allowing to obtain a less Na+ containing product even if with a lower ammonium concentration and recovery yield (part of the ammonium is lost in the first Na+ rich fraction). The optimized fractioned desorbed product (from BV 5 to 9) has the following characteristics: 1020 mL of volume collected with a concentration of 1318 mg/L for N, 402 mg/L for Ca2+, 21 mg/L for Mg2+ and only 36 mg/L for Na+.

**Figure 3.** Optimised fractioned desorption. BT7, EBCT=20 min and different desorbing solutions.

**4. Conclusions**

Geopolymer G13 proved to be a good adsorbent material for N recovery. It showed a stable behavior during repeated breakthrough cycles, good adsorption and desorption yields and an elevated operating capacity.

A preliminary optimization of operating parameters was successfully carried out, but more tests are needed in order to further optimize the whole process, especially the desorption step, in order to obtain a N concentrated solution suitable for agricultural purposes.

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