

**Development of an ion exchange process for ammonium removal and recovery
from municipal wastewater based on a metakaolin K-based geopolymer**

SUPPLEMENTARY MATERIAL

Table S1

Adsorption isotherm tests

Isotherms were performed in 250-mL glass bottles using the actual Falconara TMWW and the NH₄Cl synthetic solution. The sorbent concentration was 2.0 g_{dry solid} L⁻¹ and initial N concentrations between 10 and 440 mg_N L⁻¹ were tested. Bottles were placed in a rotatory shaker (200 rpm, 20-22°C) for 7 h. The duration of the experiment was defined based on the results of preliminary kinetic tests (data not shown). In order to obtain a negligible dilution of the competing anions (< 1%), the desired N initial concentrations were attained by mixing 100 mL of MWW with 0.005±1 mL of different NH₄Cl solutions.

In each test the equilibrium N concentration in the solid phase, $C_{S,eq}$ (mg_N g_{dry solid}⁻¹), was determined as:

$$C_{S,eq} = \frac{(C_{L,0} - C_{L,eq}) \cdot V_L}{m_S}$$

where m_S is the mass of dry adsorbent (g_{dry solid} L⁻¹), $C_{L,0}$ and $C_{L,eq}$ the initial and final NH₄-N concentration in the liquid phase (mg_N L⁻¹) and V_L the liquid volume (L). Each test was performed in triplicates and the 95% confidence intervals associated to $C_{S,eq}$ were calculated from the standard deviation of the mean values.

Experimental isotherms were interpolated by means of the Langmuir and Freundlich models:

$$\text{Langmuir} \quad C_{S,eq} = \frac{C_S^\infty \cdot C_{L,eq}}{\frac{1}{K_{eq}} + C_{L,eq}}$$

$$\text{Freundlich} \quad C_{S,eq} = K_F \cdot C_{L,eq}^{1/n}$$

where: $C_{S,eq}$ (g_N/g_{dry resin}) and $C_{L,eq}$ (g_N/L) indicate respectively the amount of sorbed N-NH₄⁺ per unit mass of adsorbent and the N-NH₄⁺ concentration in the liquid phase at equilibrium; C_S^∞ (g_N/g_{dry resin}) the maximum amount sorbed per unit mass of adsorbent, corresponding to a complete monolayer on the adsorbent surface; K_{eq} (L_{pore volume}/mg_N) the constant related to the affinity between the binding sites and N-NH₄⁺; K_F (mg_N^{1-1/n} L^{1/n} g_{dryresin}⁻¹) the sorption capacity in the Freundlich model; $1/n$ (-) the sorption intensity in the Freundlich model.

The model parameters were estimated by non-linear least squares regression of the calculated solid phase concentrations ($C_{S,eq,calc,i}$) to the corresponding experimental values ($C_{S,eq,i}$). The best-fitting model was selected on the basis of the correlation coefficient R^2 , defined so as to take into account the number of model parameters:

$$R^2 = 1 - \frac{\left(\frac{\sum_{i=1}^N (C_{S,eq,i} - C_{S,eq,calc,i})^2}{N-P-1} \right)}{\left(\frac{\sum_{i=1}^N (C_{S,eq,i} - C_{S,eq,m})^2}{N-1} \right)}$$

where N indicates the number of experimental tests in the studied isotherm, and P the number of model parameters.

Table S2

Adsorption breakthrough curves: operational conditions and simulation with the Thomas model

The lab-scale continuous flow breakthrough tests (BT) were carried out in a PVC column with a total volume of 0.144 L, a total height of 1.0 m and an inner diameter of 21 mm, packed with G13. The geopolymer was added up to a 60-cm bed height, the minimum value generally used in full-scale processes. G13 was activated in K^+ form by eluting 10 bed volumes (BVs) of a 100 g L^{-1} KCl solution.

A characterization of the fluid dynamic behavior of the adsorption bed was carried out in the EBCT range used in the BT tests (5÷10 min) by means of frontal analysis tests conducted with KCl 5% w/v. Additional fluid dynamic tests were carried out after each adsorption experiment to verify the stability of the bed packing quality. Electrical conductivity (EC) was measured at the column outlet with a CO11 conductivity probe (VWR, Radnor, Pennsylvania, USA).

In all the adsorption tests, NH_4 -spiked TMWW was fed downstream in the column with a Masterflex L/S 0.1 HP 1-100 rpm peristaltic pump (Avantor, Radnor, PA, US). Pressure drop and flowrate were measured hourly. Outlet samples were taken every 30 minutes, inlet samples were taken every 3 h. Cation outlet concentrations were normalized by the average inlet concentration.

The adsorption operational conditions were selected on the basis of the following elements: i) the pH was the natural one of the tested MWWs (7.9); ii) temperature was maintained constant at 22°C through a jacket connected to a temperature-controlled bath; iii) the empty bed contact time (EBCT) was varied in the 5-10 minute range, in order to find a compromise between the reduction in column size attainable with low EBCTs and the risk to reduce ion exchange performances due to an excessive increase of the non-equilibrium mass transfer zone in the column.

The NH_4^+ adsorption breakthrough curves were simulated by means of the Thomas model:

$$C_L(x, t) = \frac{C_{L,0}}{1 + e^{\left[C_{S,eq} \cdot m \cdot \frac{x}{L} - C_{L,0} \cdot Q \cdot t + C_{L,0} \cdot BV \cdot \varepsilon \cdot \frac{x}{L} \cdot \frac{K_{Th}}{Q} \right]}}$$

where $C_L(x, t)$ and $C_{L,0}$ ($mg_N L^{-1}$) are respectively the N- NH_4^+ liquid-phase concentrations at height x (m) in the column at time t (h) and the average concentration fed to the column during the test, m (g_{dry}) the mass of dry resin packed in the column, x (m) the zeolite bed height in a generic point of the column, L (m) the maximum zeolite bed height (0.60 m), Q ($L h^{-1}$) the flowrate fed to the column, BV (L) the resin bed volume, ε (-) the effective porosity of the packed bed, $C_{S,eq}$ ($mg_N g_{dry resin}^{-1}$) the resin capacity at saturation (i.e. in equilibrium with $C_{L,0}$) and K_{Th} ($L h^{-1} mg^{-1}$) the Thomas rate constant. The best-fitting values of $C_{S,eq}$ and K_{Th} were estimated using the Solver add-in in Microsoft Excel, using for the other parameters input values derived from experimental measurements or from elaboration of the fluid-dynamic tests.

Table S3

Analytical methods and determination of cation exchange capacity

Cation analysis were performed with an HPIC method using an Integrion ion chromatograph (ThermoFisher Scientific, Waltham, Massachusetts, USA) equipped with an IonPacTM CS12A-8 μ m 4 x 250 mm column, a CG12A-8 μ m 4 x 50 mm guard column and an Electrolytically Regenerated Suppressor CDRS600 4 mm. The eluent was 20 mM methanesulfonic acid at 1 mL min⁻¹ and 30°C. pH was measured by employing a pH glass electrode with built-in temperature sensor connected to a MU 6100 L multi meter (VWR, Radnor, Pennsylvania, USA). The relative average experimental errors, estimated by means of a statistical elaboration of repeated analyses of check standards, resulted equal to 1% for cation concentrations and 3-4% for the other parameters.

The total cation exchange capacity (CEC) of G13 geopolymer was assessed in a 10-cm high column in which the sorbent – previously packed and conditioned in the desired form – was saturated initially with a 2N solution of NH₄Cl (28 g_N L⁻¹, a concentration 700 higher than the typical NH₄⁺ concentration in municipal wastewater), and then with a 2N solution of KCl. All chemicals were provided by Sigma-Aldrich (Milano, Italy).

Table S4

Best estimates of the parameters relative to the fitting with the Thomas model (Table S3) of the breakthrough tests conducted with geopolymers G13, with Falconara (FA) or Bologna (BO) WWTP effluent, at EBCTs varying in the 5-10 min range. The operational conditions and performance parameters relative to each test are reported in Table 4.

Test ID	$C_{s,eq}$ $\text{mg}_N \text{ g}_{\text{dry resin}}^{-1}$	K_{Th} $\text{L h}^{-1} \text{ mg}^{-1}$	R^2
FA-10a	12.3±0.1	0.0047±0.0002	0.989
FA-10b	11.8±0.2	0.0045±0.0006	0.985
FA-10c	10.6±0.1	0.0053±0.0002	0.990
FA-7.5	12.1±0.1	0.0058±0.0003	0.994
FA-5	12.9±0.3	0.0070±0.0009	0.986
FA-10d	11.7±0.2	0.0036±0.0004	0.973
BO-10	11.9±0.1	0.0047±0.0004	0.992

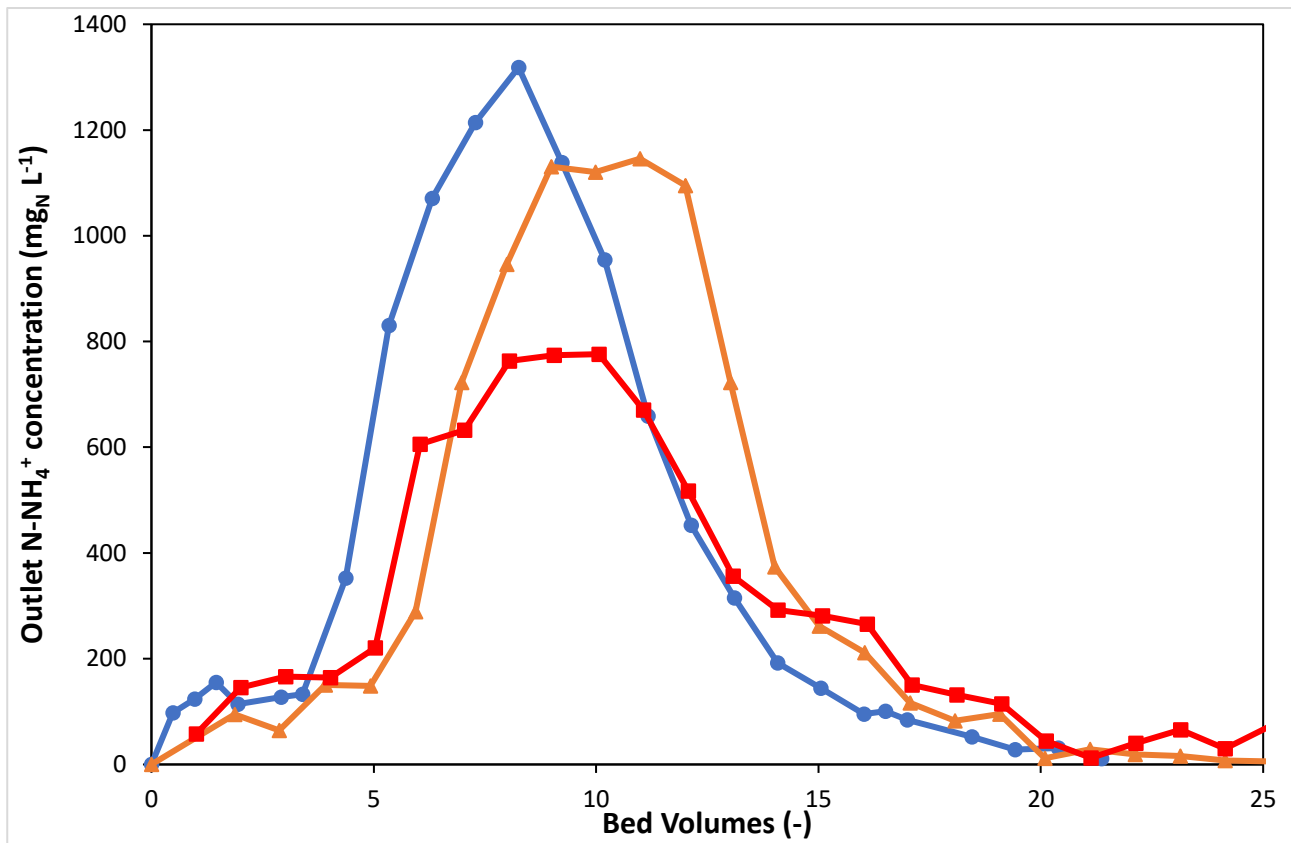


Fig. S1

Ammonium breakthrough curves, during the desorption step of tests FA-10a (blue circles), FA-10b (orange triangles) and FA-10c (red squares) conducted with KCl 10 g L⁻¹, at desorption EBCTs varying in the 20-120 min range (detailed operational conditions are reported in Table 4).