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Italiadomani
PIANO NAZIONALE DI RIPRESA E RESILIENZA

Removal and recovery of ammonium and phosphate from wastewater by means of geopolymer-based adsorbents

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CNR ISSMC

WHY PHOSPHATE RECOVERY BY ADSORPTION?

- Production of P-based fertilizers is expected to increase by 100% by 2050.
- P represents a limited resource. Unless a marked P recovery is implemented worldwide, **the peak of phosphate rock extraction is expected to be reached by 2040-50**
- Several technologies for phosphate recovery from municipal wastewater (MWW) are under development or optimization. They generally implement P recovery in the sludge line of wastewater treatment plants.
- **Adsorption** is not yet applied at full scale for P recovery, **but it represents an interesting option for P recovery both from the sludge line and wastewater line**.

WHY AMMONIUM RECOVERY BY ADSORPTION?

- Production of N-based fertilizers is expected to increase by 50% by 2050, starting from the current level of 110 million t/year.
- N is not a limited resource, but **ammonia production from atmospheric N_2 is a very energy-intensive process** (about 8000 kWh / t of NH_3 produced)
- In addition, **the traditional biological process for NH_4^+ removal from MWW is energy intensive** (3300-3500 kWh / t NH_4^+ removed) and does not allow any N recovery
- **NH_4^+ recovery from MWW by adsorption, followed by the production of N-based fertilizers, represents an attractive option**, capable to drastically cut the energy requirement for both NH_4^+ removal from MWW and N-based fertilizers production

THE GOAL OF THIS RESEARCH IS …

… to develop and validate with real wastewater:

- **Innovative geopolymers for the removal of ammonium by cation exchange** from MWW and from effluents produced in the sludge treatment line
- **Innovative geopolymer / hydrotalcite composites for the contemporary removal of ammonium (by cation exchange) and phosphate (by adsorption / anion exchange)** from MWW and from effluents produced in the sludge treatment line

TESTED SORBENTS

Pure geopolymers for NH_4^+ removal:

- K-G2: K-based geopolymer with Si:Al ratio = 2
- Na-G1.2: Na-based geopolymer with Si:Al ratio = 1.2

Pure hydrotalcites for PO_4^{3-} removal:

- S911 → Sorbacid 911: $[Mg_2Al_3(OH)_{2(2+x)}]CO_3 \cdot nH_2O$
- P61 → Pural 61: 61% MgO, 39% Al_2O_3
- P70 → Pural 70: 70% MgO, 30% Al_2O_3
- P50 → Pural 50: 50% MgO, 50% Al_2O_3

Geopolymer / hydrotalcite composites for contemporary NH_4^+ & PO_4^{3-} removal:

- K-G2 90% - S911 10%
- K-G2 90% - P61 10%
- K-G2 65% - P70 35%

All tests were conducted with the 2 types of ACTUAL WASTEWATER:

	WWTP effluent → N&P removal from the wastewater line	Sludge WW from centrifugation of digested municipal sludge → N&P removal from the sludge line
TSS (mg/L)	5.3 ± 0.6	0.3 ± 0.1
NH_4-N (mg/L)	40 ± 3	810 ± 21
PO_4^{3-}-P (mg/L)	7 ± 1	122 ± 12
Na^+ (mg/L)	48 ± 3	120 ± 7
K^+ (mg/L)	11 ± 1	230 ± 4
Mg^{2+} (mg/L)	21 ± 2	3.4 ± 0.5
Ca^{2+} (mg/L)	14 ± 1	39 ± 1
Cl^- (mg/L)	128 ± 15	221 ± 3
NO^{3-} (mg/L)	0.81 ± 0.02	9.6 ± 0.2
SO_4^{2-} (mg/L)	93 ± 6	14 ± 2
pH	7.6 ± 0.2	6.6 ± 0.4

The tested WWs were pre-treated by microfiltration at 1 µm to avoid clogging of the packed adsorption columns

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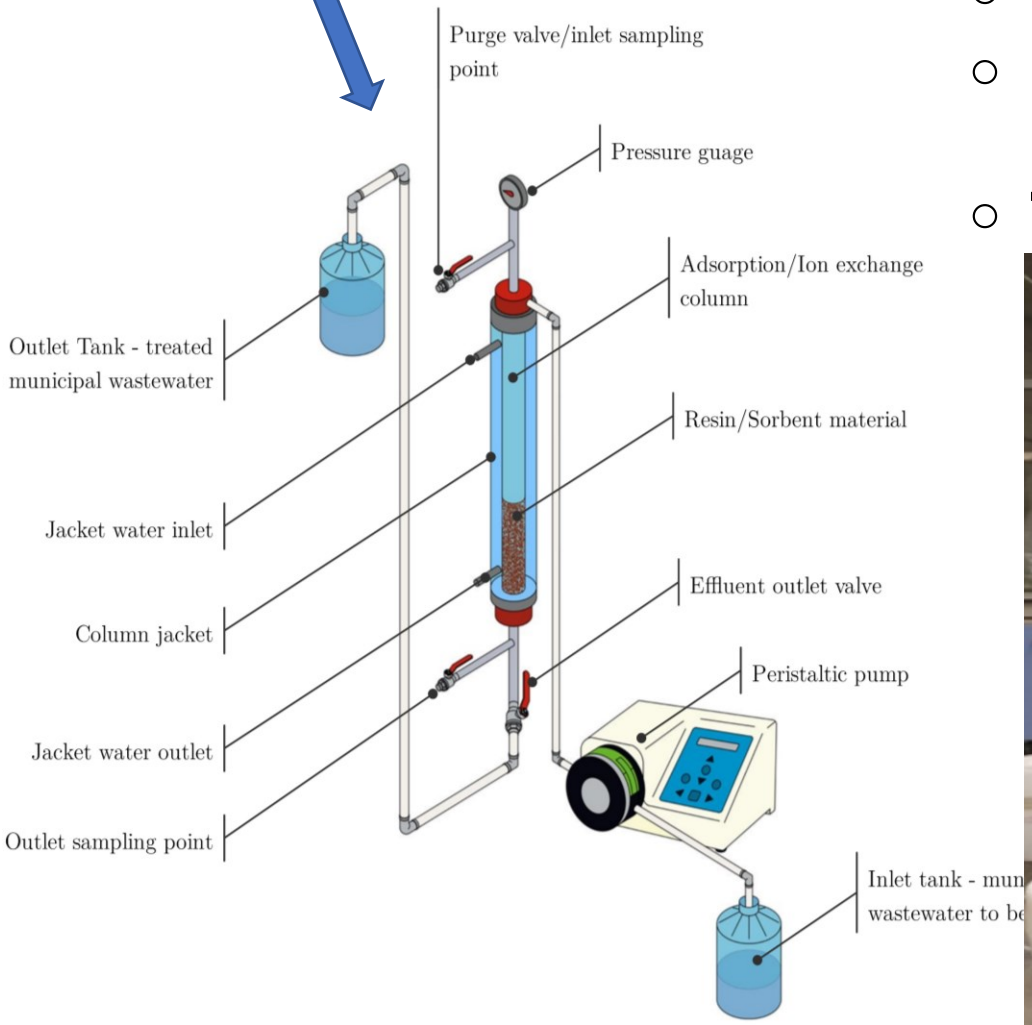
BATCH AND CONTINUOUS FLOW TESTS SETUP

- 125 mL borosilicate glass bottles
- Sorbent concentration: 2-5 $g_{dry\ sorbent}/L$
- Operating parameters:
  - orbital shaker 160 RPM
  - Temperature 22°C
  - Equilibrium time 24 h



- Resin bed height: 20-30 cm
- Empty bed contact time: 10-20 min
- Temperature: 22°C

1) AMMONIUM REMOVAL WITH PURE GEOPOLYMERS

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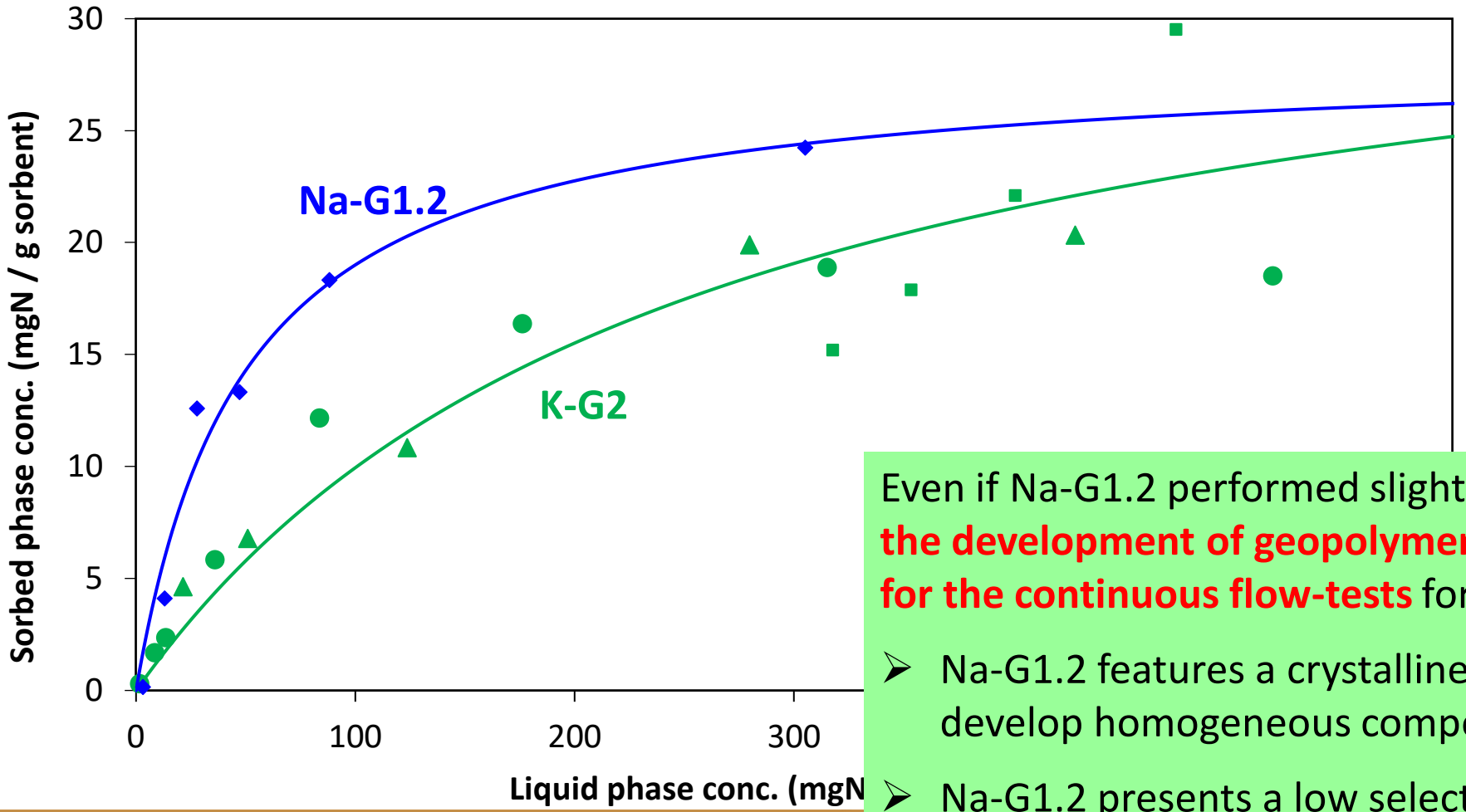
AMMONIUM REMOVAL WITH PURE GEOPOLYMERS: BATCH ISOTHERMS



- Tests were conducted with sludge WW
- Experimental data + best-fitting Langmuir interpolation:

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

Even if Na-G1.2 performed slightly better, **K-G2 was selected for the development of geopolymer / hydrotalcite composites and for the continuous flow-tests** for several reasons:

- Na-G1.2 features a crystalline phase that makes it difficult to develop homogeneous composites
- Na-G1.2 presents a low selectivity for ammonium in comparison to the other cations

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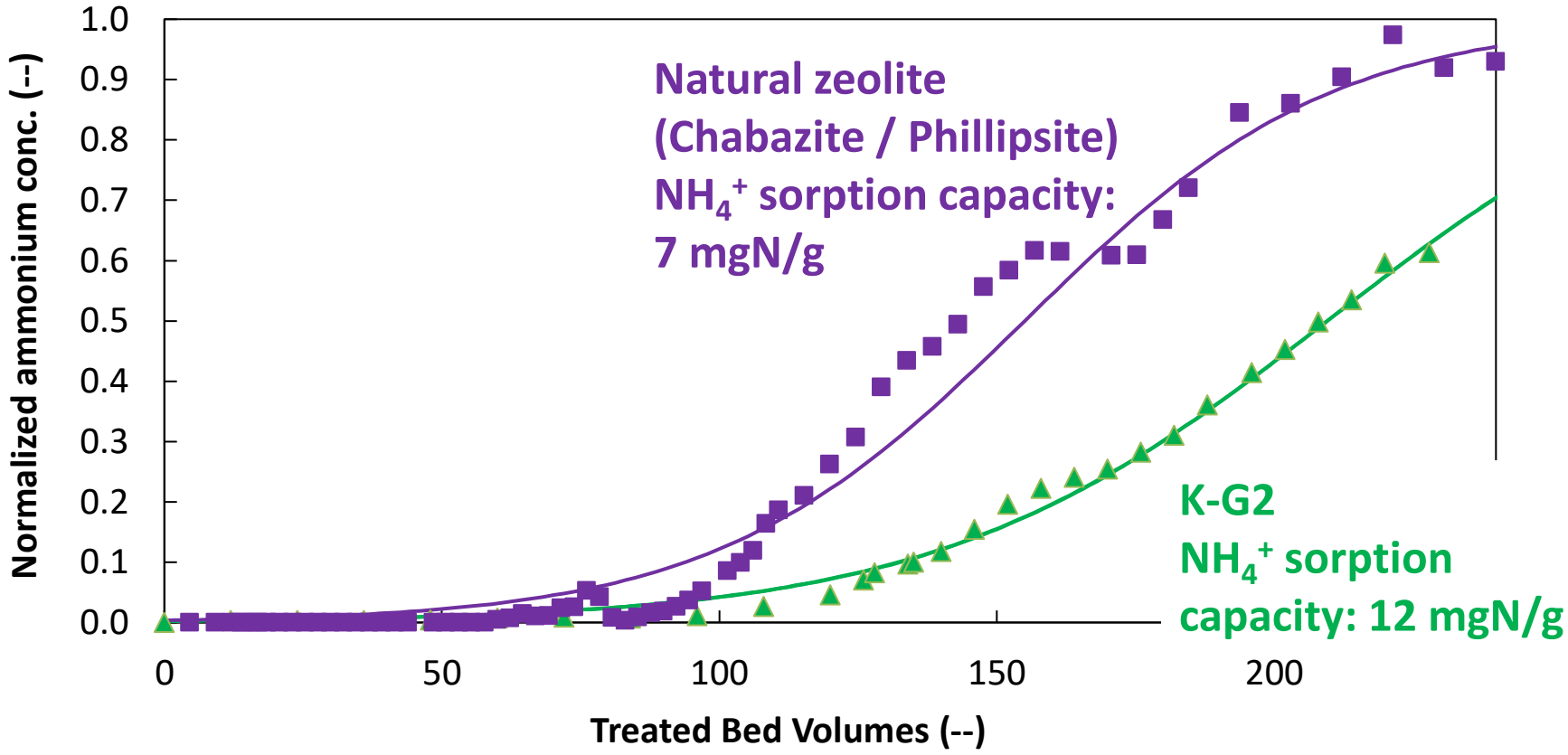
AMMONIUM REMOVAL WITH GEOPOLYMER K-G2: CONTINUOUS FLOW TESTS

a) Geopolymer K-G2 compared to a natural zeolite, tests conducted with WWTP effluent (40 mgN/L)

- **Empty Bed Contact Time (EBCT): 10 min**
- **Resin bed height: 20-30 cm**



2) SIMULTANEOUS AMMONIUM & PHOSPHATE REMOVAL WITH GEOPOLYMER / HYDROTALCITE COMPOSITES

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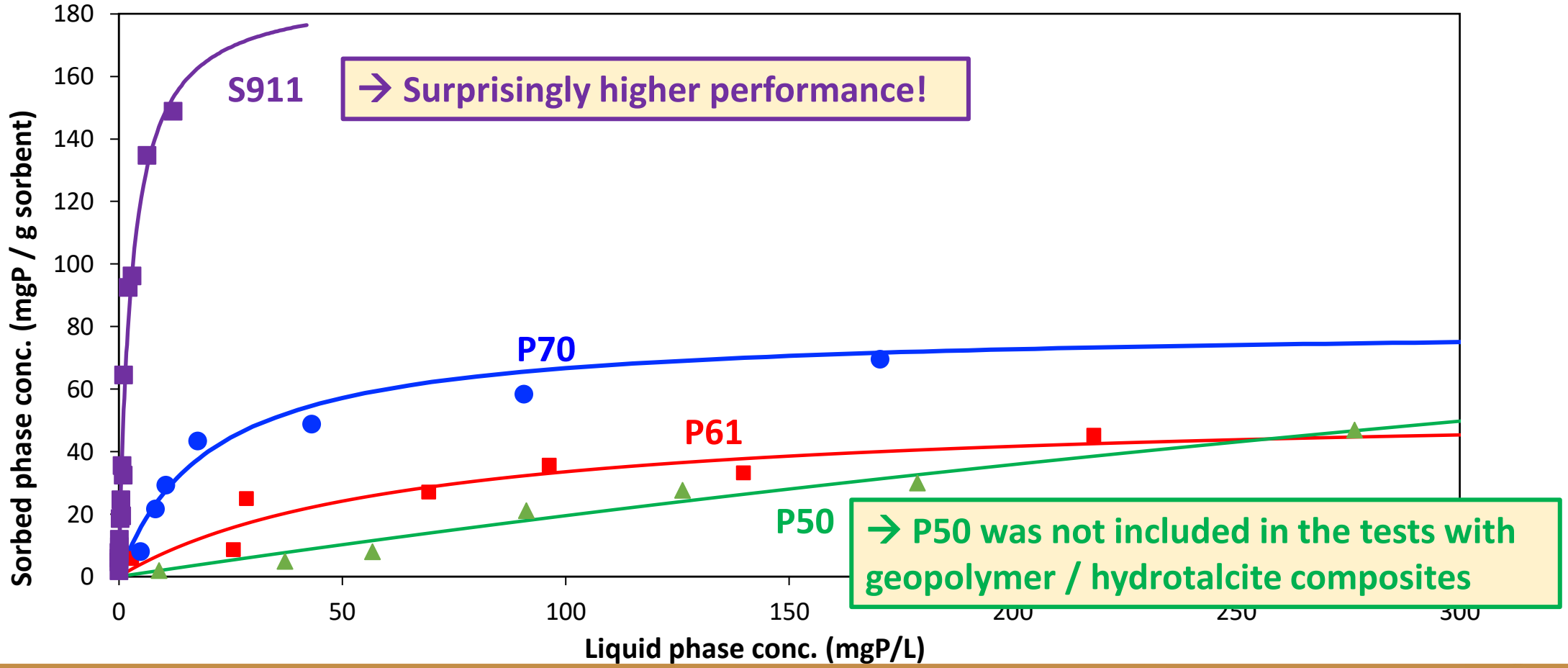
PHOSPHATE REMOVAL WITH GEOPOLYMER / HYDROTALCITE COMPOSITES: BATCH ISOTHERMS FOR THE PRELIMINARY SCREENING OF DIFFERENT HYDROTALCITES



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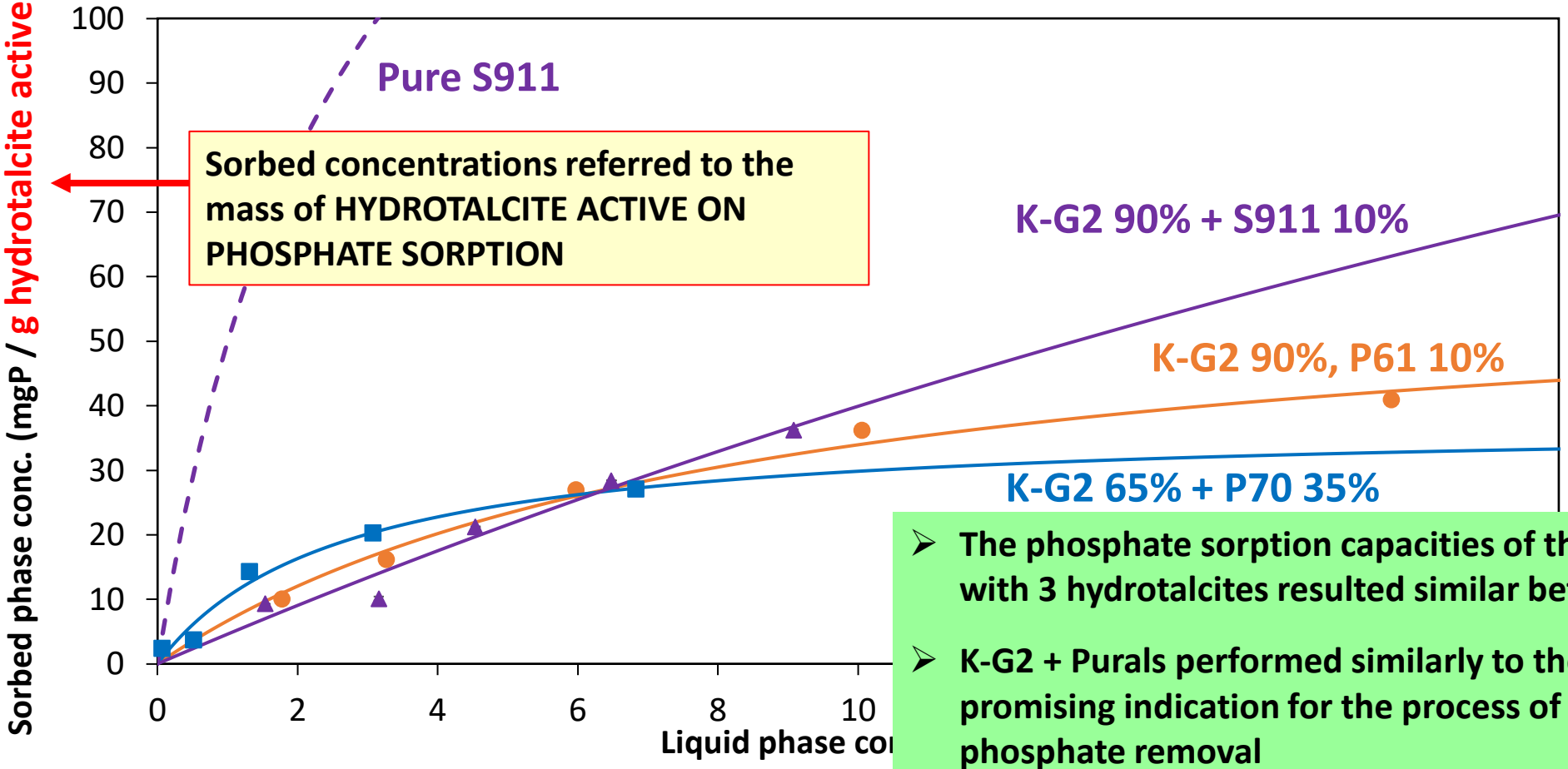
PHOSPHATE REMOVAL WITH GEOPOLYMER / HYDROTALCITE COMPOSITES: BATCH ISOTHERMS



Sorbed phase P concentrations in equilibrium with 7 mgP/L in the liquid phase (mgP/g):

K-G2 + 35% P70	27
K-G2 + 10% S911	29
K-G2 + 10% P61	28
Pure P70	21
Pure S911	120 !

- The phosphate sorption capacities of the composites of geopolymer with 3 hydrotalcites resulted similar between each other
- K-G2 + Purals performed similarly to the corresponding pure Purals → promising indication for the process of contemporary ammonium & phosphate removal
- K-G2 + S911 performed worse than pure S911

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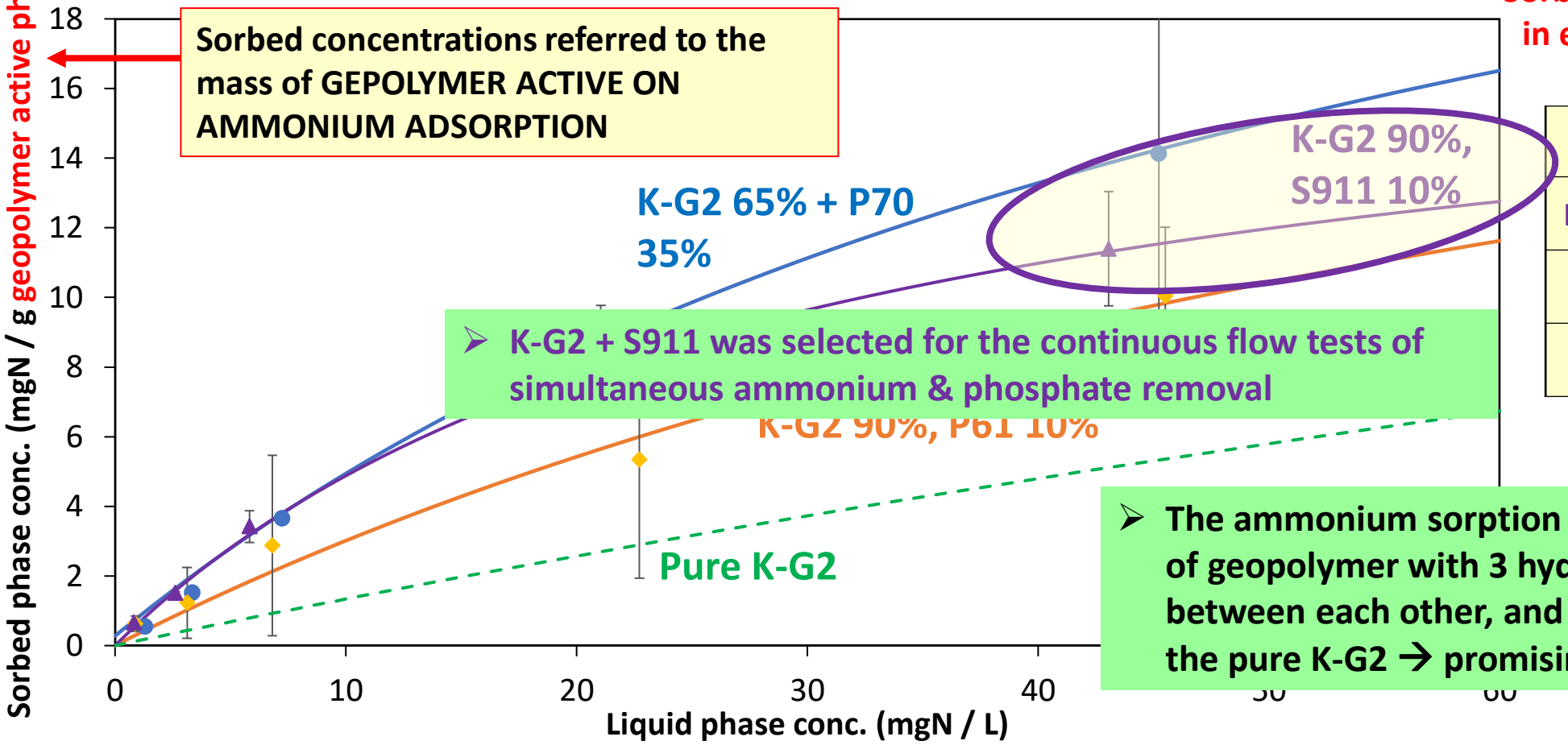
AMMONIUM REMOVAL WITH GEOPOLYMER / HYDROTALCITE COMPOSITES: BATCH ISOTHERMS

Sorbed concentrations referred to the mass of GEPOLYMER ACTIVE ON AMMONIUM ADSORPTION



➢ K-G2 + S911 was selected for the continuous flow tests of simultaneous ammonium & phosphate removal

Sorbed phase NH_4^+ concentrations in equilibrium with 40 mgN/L in the liquid phase (mgN/g):

K-G2 + 35% P70	13
K-G2 + 10% S911	11
K-G2 + 10% P61	9
Pure K-G2	5

➢ The ammonium sorption capacities of the composites of geopolymer with 3 hydrotalcites resulted similar between each other, and slightly higher than that of the pure K-G2 → promising indication!

CONTINUOUS FLOW TESTS OF SIMULTANEOUS AMMONIUM & PHOSPHATE REMOVAL WITH THE K-G2 + S911 COMPOSITE…

… IN PROGRESS!

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CONCLUSIONS

- **The K-based geopolymer resulted a promising material for ammonium removal & recovery from both MWW (40 mgN/L) and sludge WW (810 mgN/L)**, on both batch and continuous flow tests
- **Composites formed by the K-based geopolymer and 3 hydrotalcites led to promising results in terms of simultaneous ammonium & phosphate removal in batch isotherms**. Sorption capacities for both N & P resulted comparable to those of the corresponding pure materials, except for the surprisingly high performance of Sorbacid 911 alone
- Further research is needed to optimize the continuous flow adsorption / desorption process of simultaneous ammonium and phosphate removal

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GEopolymer based Adsorbents

GEA - GEopolymer based Adsorbents for effective adsorption and selective separation of CO_2 and eutrophication pollutants

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