DuRSAAM Symposium
08-10 February 2023 | Ghent - Belgium

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REMOVAL OF AMMONIUM FROM WASTEWATER WITH METAKAOLIN BASED-GEOPOLYMER SORBENTS

M. Otero, L. Freire, S. Gómez-Cuervo, P. Villar, R.Abal*

AIMEN Asociación de Investigación Metalúrgica del Noroeste

aimen TECHNOLOGY CENTRE

Life
LIFE Climate Change Adaptation

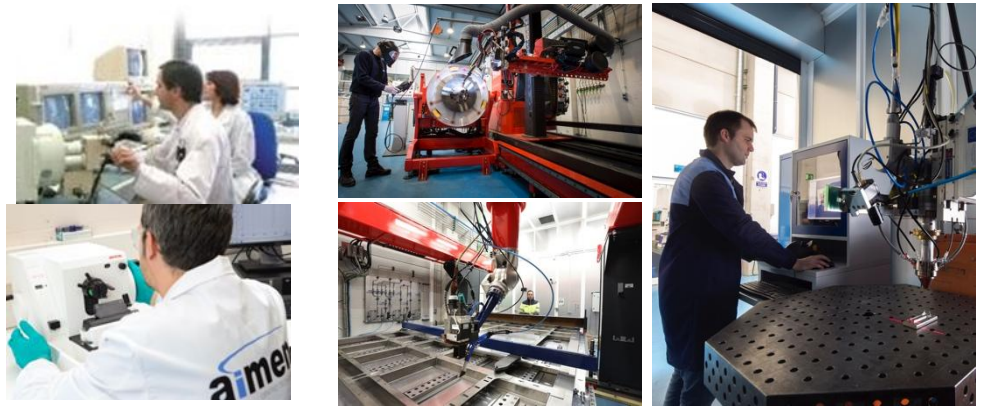
LIFE GREEN ADAPT
Green and Nature-Based Solutions for climate change-resilient waste infrastructure

Marie Curie Innovative Training Network
H2020-MSCA-ITN-2018-813596

GHENT UNIVERSITY, TU Delft, KIT Karlsruhe Institute of Technology, The University of Sheffield., University of Patras, ETH zürich

AIMEN (Technology centre)

Testing & Analysis | **Industrial Services** | **R&D&i**



690 R&D&i Projects In the last 10 years

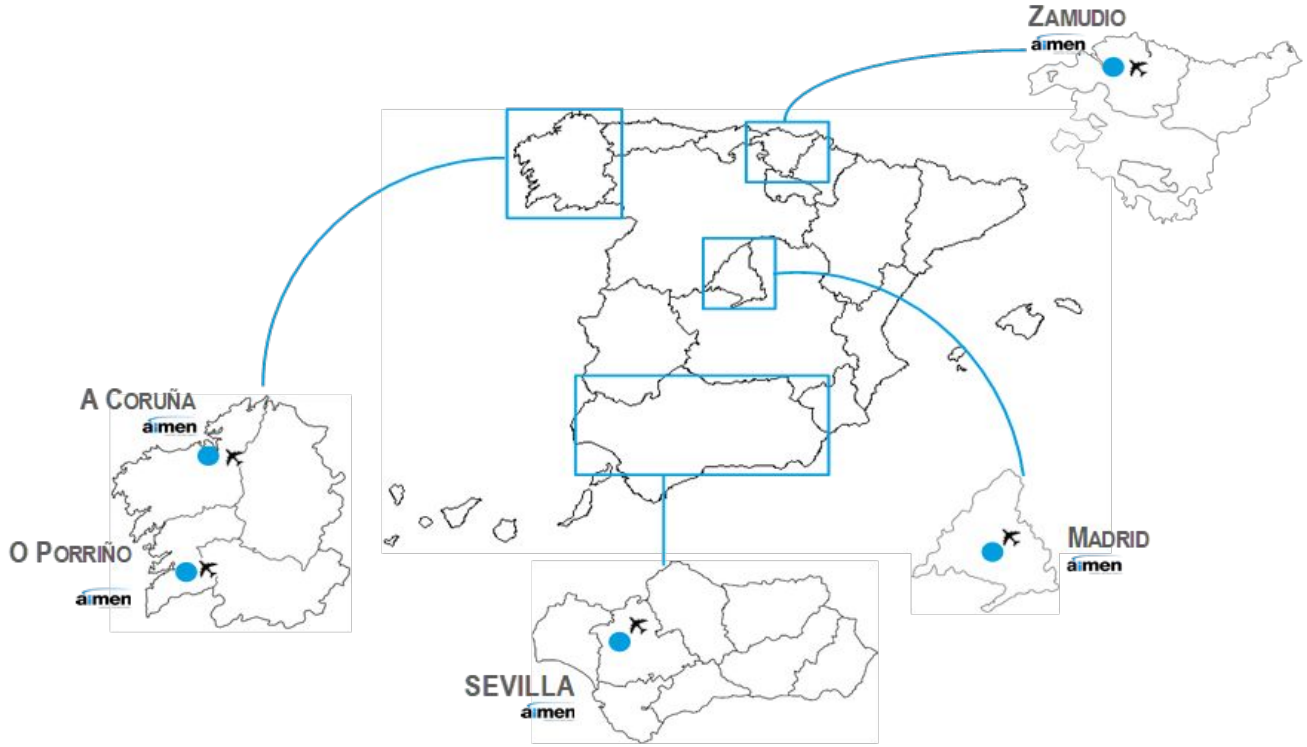
6 Active Patents As of 31/12/2020

+750 Clients Annual average In the last 5 years

250 Employees 39 PhDs 61% men 39% women

15,6 M€ Anual Income 2019

292.435 Technical Reports As of 31/12/2020



Experts in
- Laser technologies
- Industrial robotics
- Environmental approaches
- **Advanced materials**

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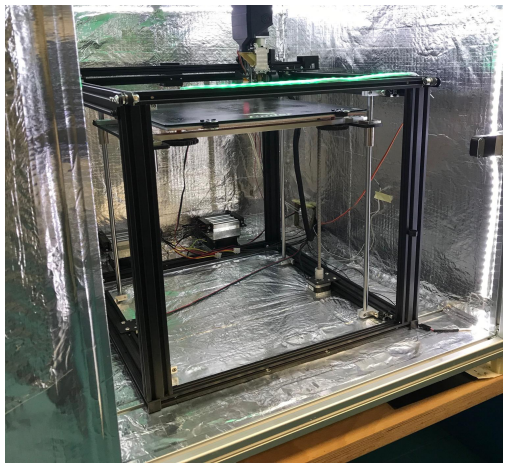
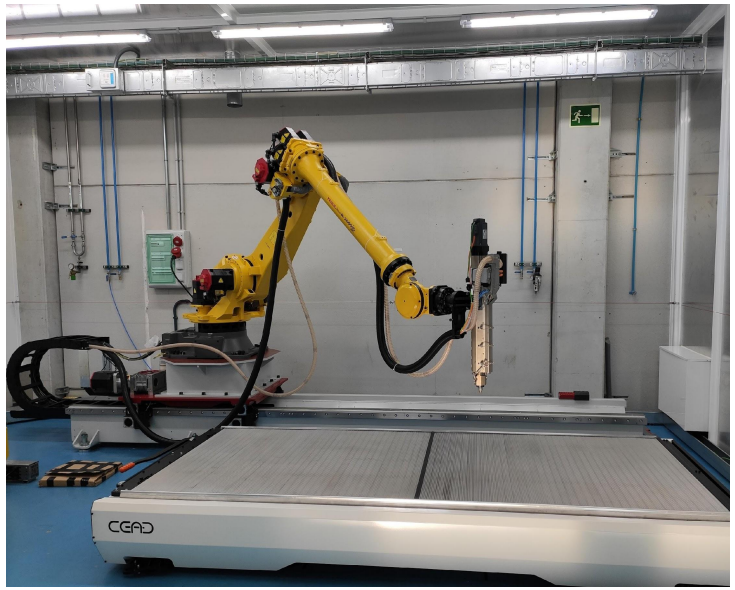
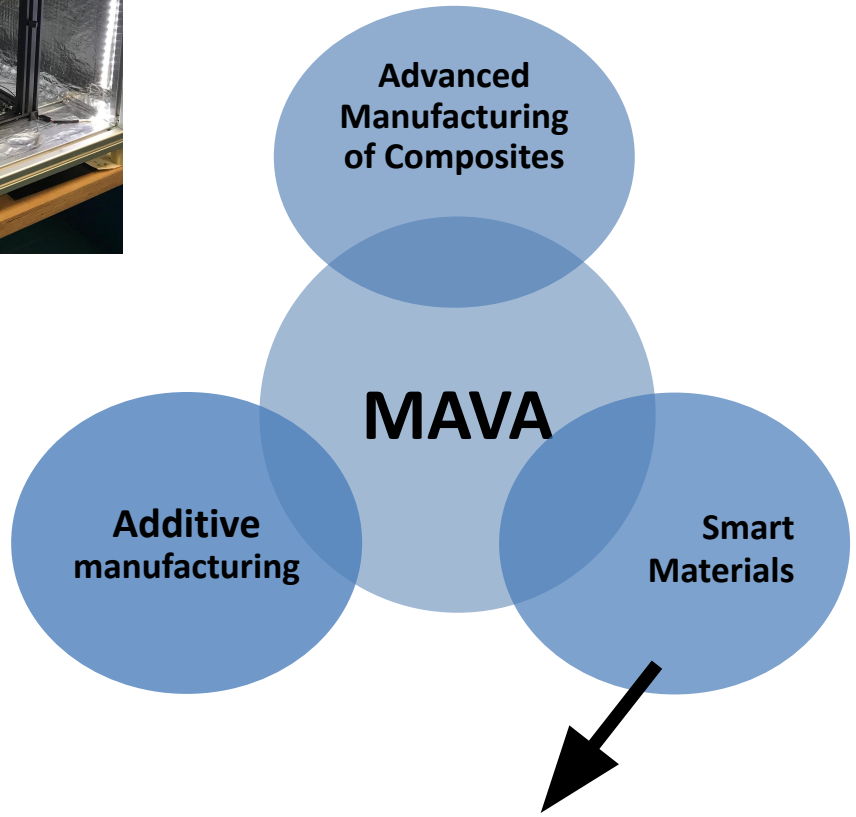
MAVA (Advanced materials)







Alkaline Activated Technology line

AAT In AIMEN

2015 — 2023 .....

Raw materials

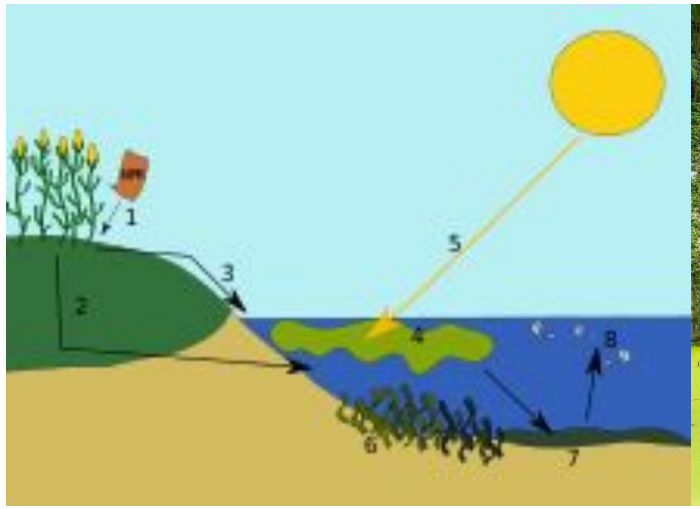
- ❑ Solid precursors: Slags, fly ashes, MK, CDW, red muds…
- ❑ Alkaline activators: SS, KS, solid activators…

Aplicattions:

- ❑ Adsorbents
- ❑ Insulating panels
- ❑ Managment of radioactive wastes
- ❑ Building structures
- ❑ High temperature resistant structures (over 1000°C)
- ❑ Composites

Ammonium NH_4^+

- Dominant form of nitrogen pollution in water
- It causes eutrophication
  - Growth of algae on surface
  - Block the sunlight. Plants die.
  - Bacterial communites descompose the remains using up oxygen.
  - Depletion of oxygen. Fish die.



Methods NH_4^+ removal

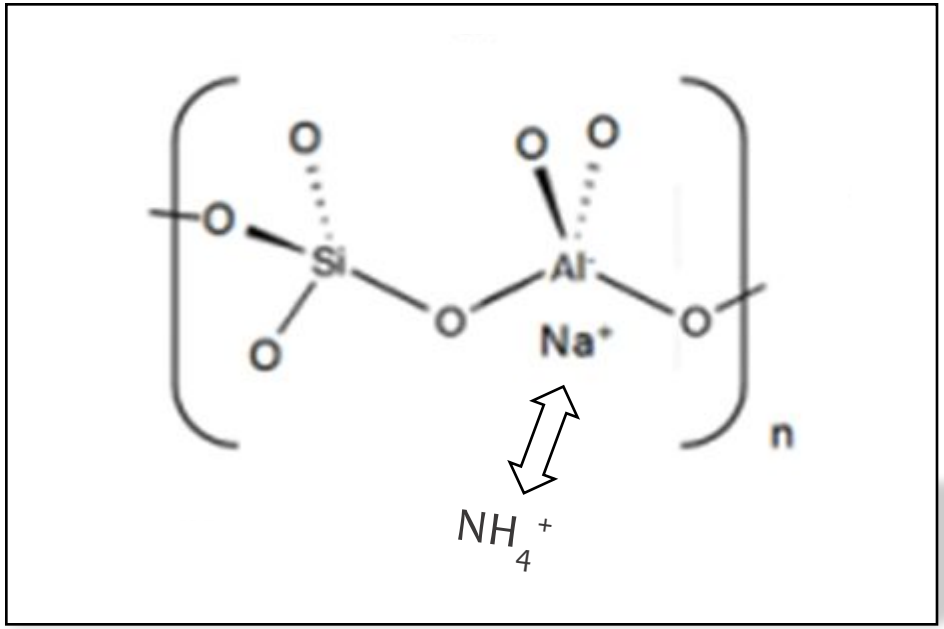
- Microbial nitrification–denitrification reactions
- Breakpoint chlorination
- Air extraction
- Reverse osmosis
- Ionic Exchange

- Microbial reactions are the most widely used. However the rates drop as the water temperature decreases. High operational costs.
- Ionic Exchange shows lower operational costs and high efficiences.
- Zeolites are the main adsorbants used in ionic Exchange methods. Synthesis requires high temperatures.
- GEOPOLYMER PROMISING ALTERNATIVE

Geopolymer as Ion Exchange adsorbent

Characteristics

- **Chemistry structure** with negative charges in the aluminum and sodium cations located on the voids.
- **Low cost adsorbent**. They do not require high synthesis conditions. Available local raw materials, mainly wastes.
- Good **mechanical properties** and **integrity in water**.



Ion Exchange process in the voids.

Geopolymer Formulations

Materials

- **Metakaolin**
- **Na_2SiO_3**: 25,6% SiO_2, 7,9% Na_2O, 66,5% H_2O
  NaOH pellets
- **Granite waste**
- **H_2O_2 30%**

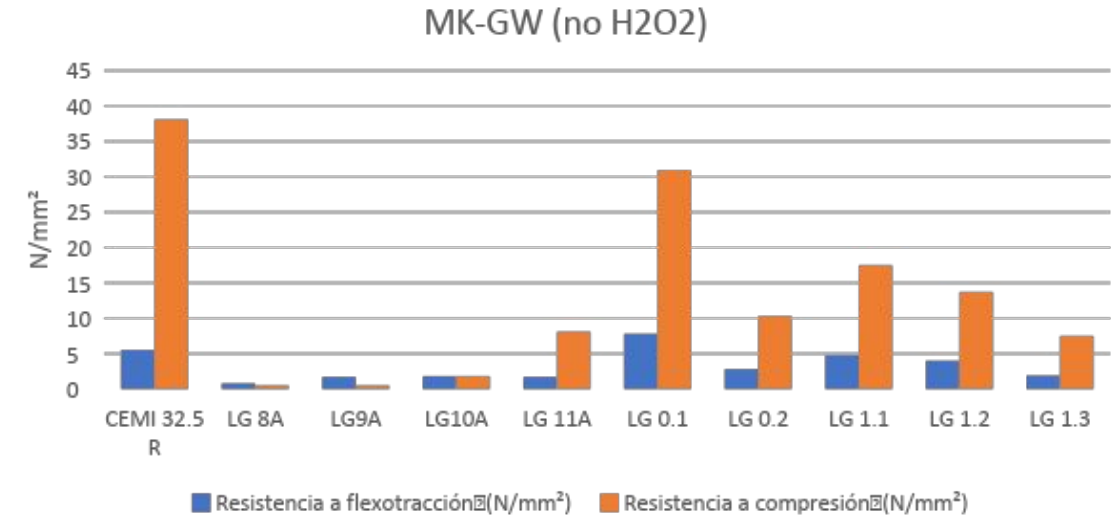
Foaming agent

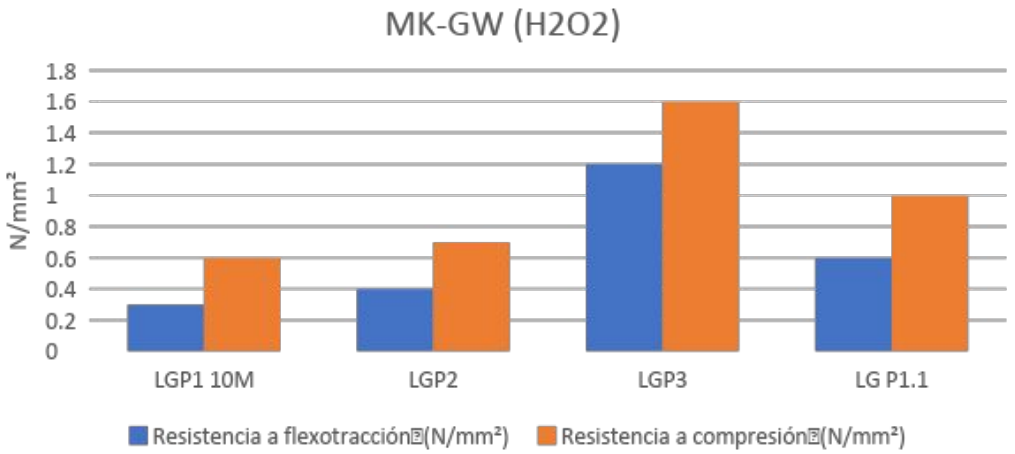
$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$$
$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^-$$

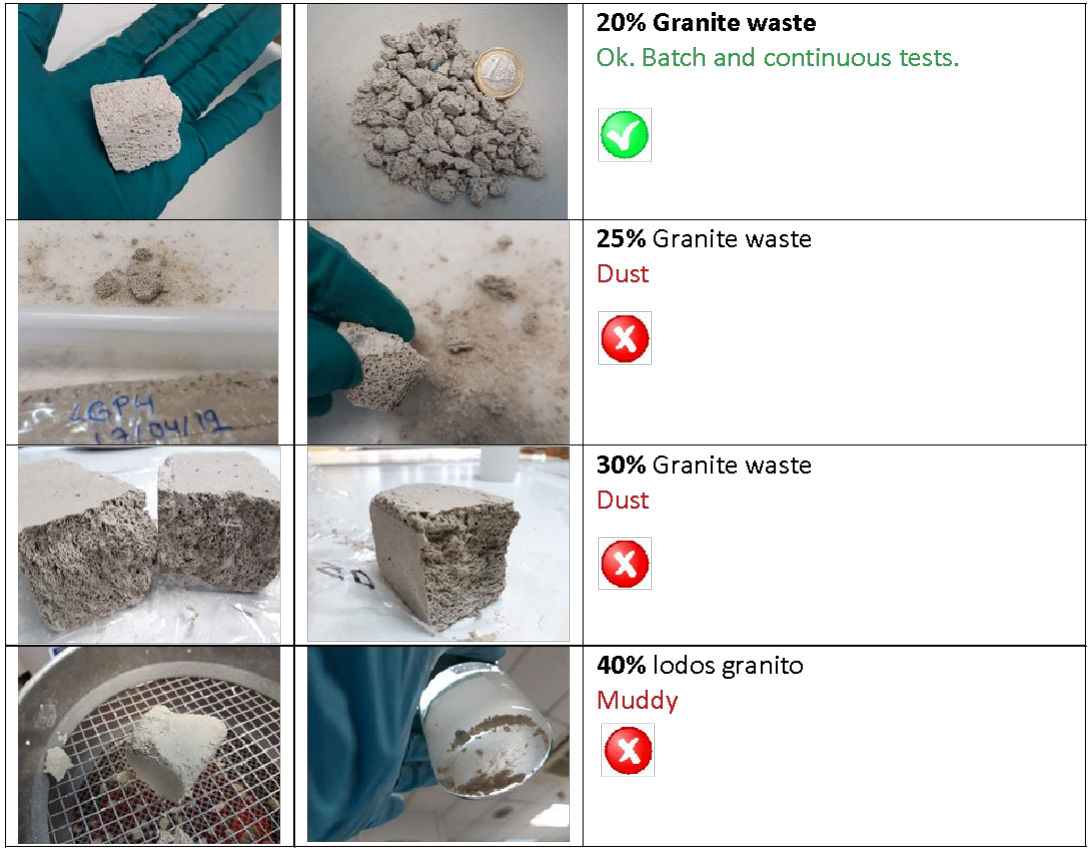
Parameters	Units	Ranges
SiO_2/Al_2O_3	Molar ratio	3.0-4.5
Sodium silicate/NaOH (Ms)	Molar ratio	0.2-0.4
NaOH	molarity	8-14
Curing temperature	°C	25-60
Granite waste	% substitution	0-60
Foaming agent (H_2O_2)	% Mass	0-3

Geopolymer characterization

Mechanical and porosity tests





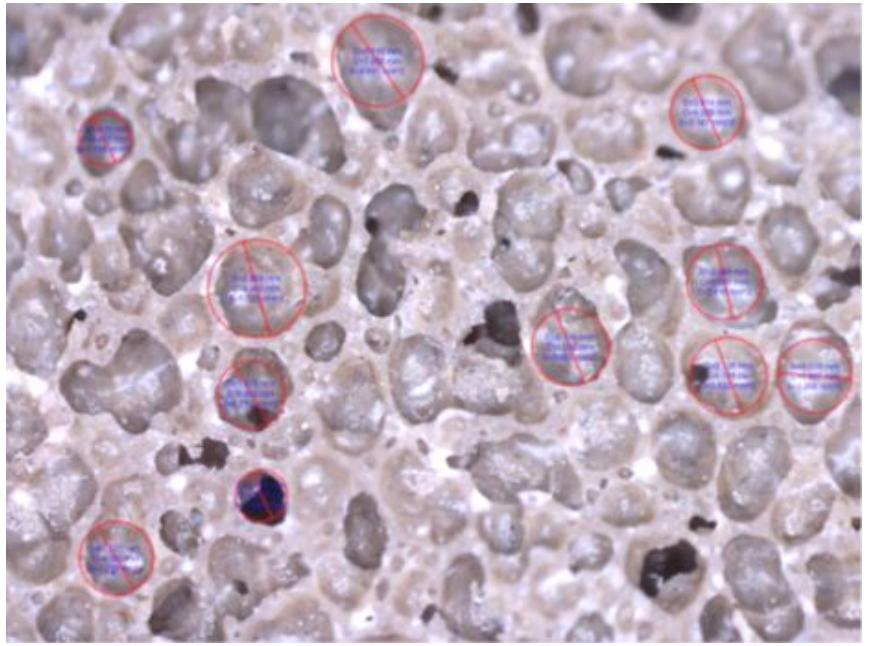


		Apparent density (g/cm3)	Bulk density (g/cm^3)	True density (g/cm3)	Total porosity
No H_2O_2 addition	LG0.1	1,56	1,51	1,98	**23,65**
	LG0.2	1,09	1,34	2,08	**35,67**
	LG1.1	1,59	1,57	1,54	**6,24**
	LG1.2	1,71	1,67	1,65	**6,21**
	LG1.3	1,82	1,78	1,76	**6,42**
H_2O_2 addition	LGP1	0,77	0,97	1,84	**47,49**
	LGP2	0,71	0,9	2,24	**59,96**
	LGP3	0,75	0,86	2,18	**60,45**

Geopolymer characterization

Final adsorbent formulation

Parameters	Units	Values
SiO_2/Al_2O_3	Molar ratio	1,5
SS/NaOH	Molar ratio	1,2
NaOH	Molarity	10
Granite waste	%Substitution	20
H_2O_2	%	1
Hardening time	Hours	24
Curing temperature	°C	25



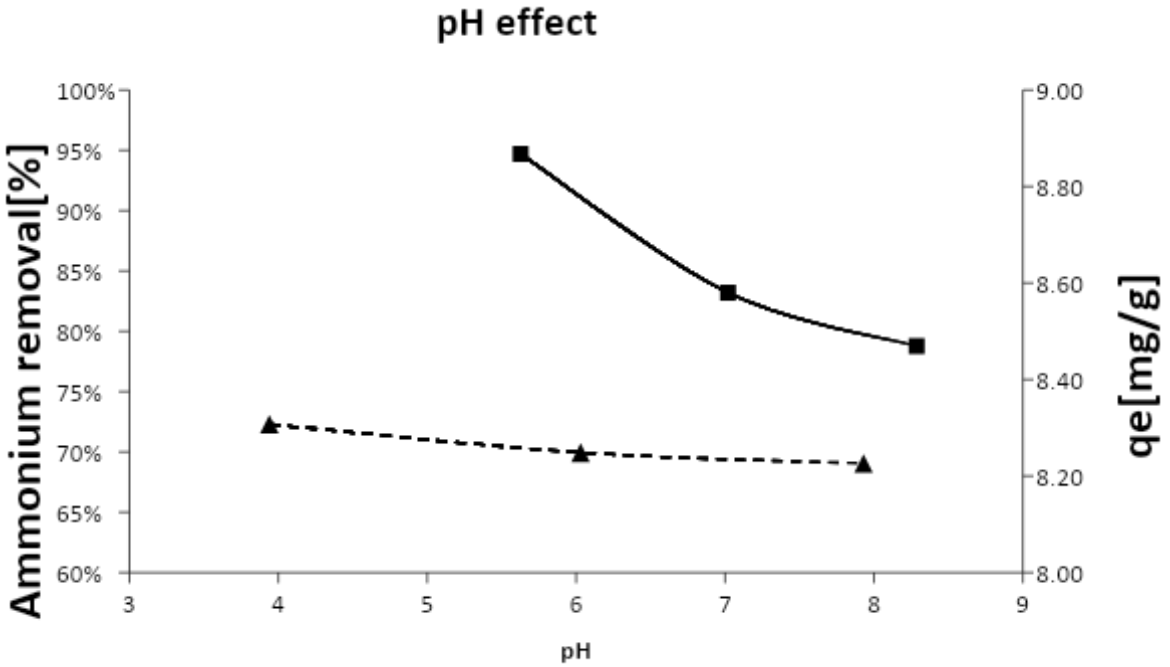
SEM image

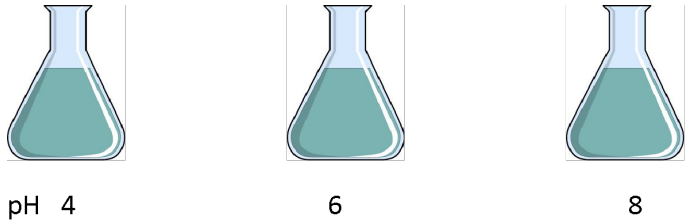
MK-20%GW-1%H_2O_2

6,1MPa compressive strength
1,6Mpa flexural strength
58,99% porosity
1-2mm pore size

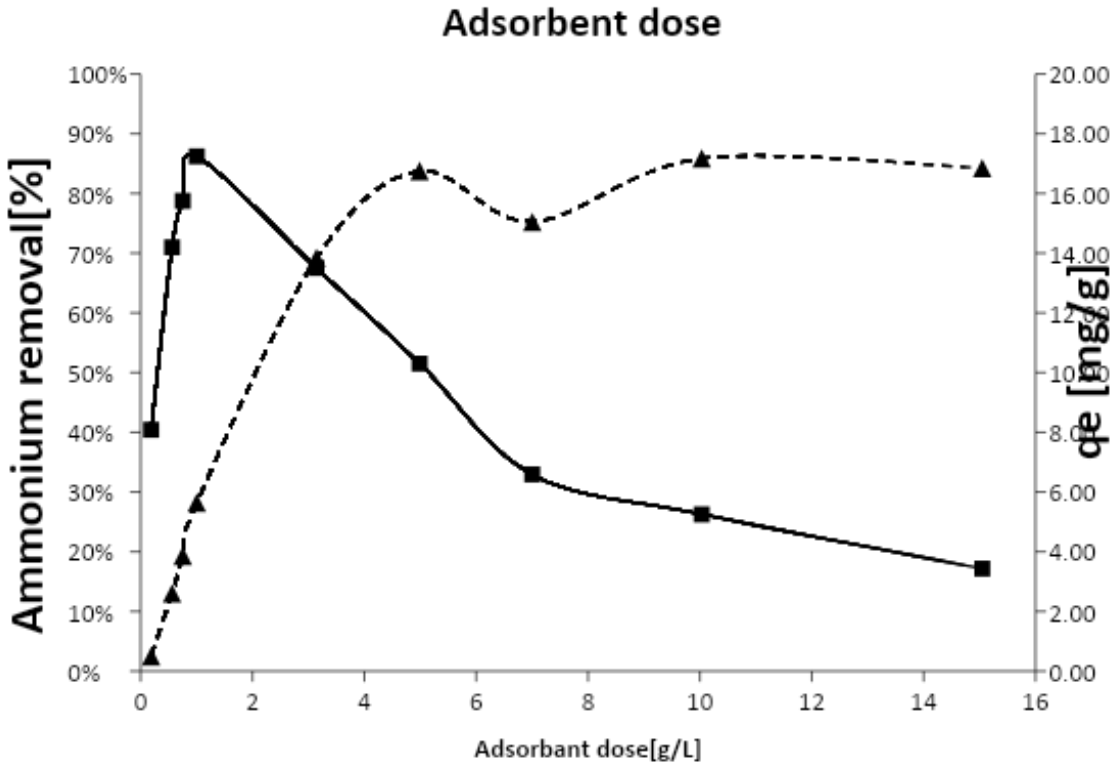
Batch tests

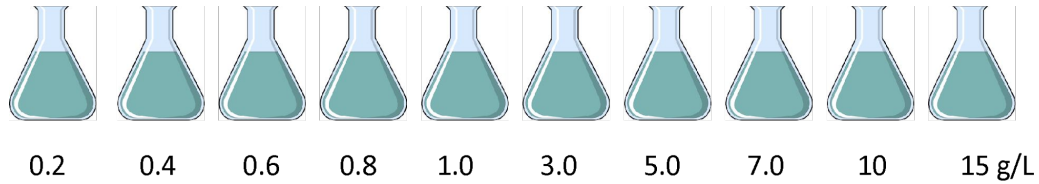
Ammonium removal %
qe: Adsorption capacity (mg adsorbate/g adsorbent)





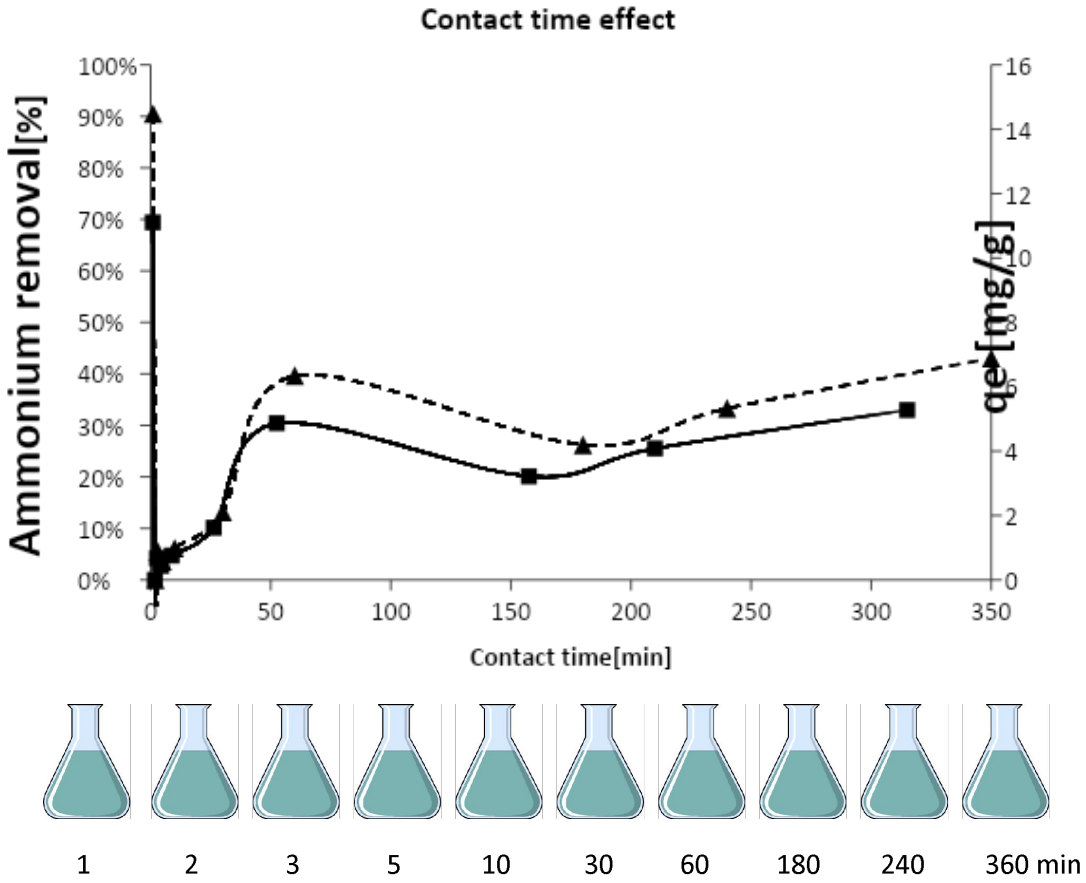
adsorption increased slightly with more acid



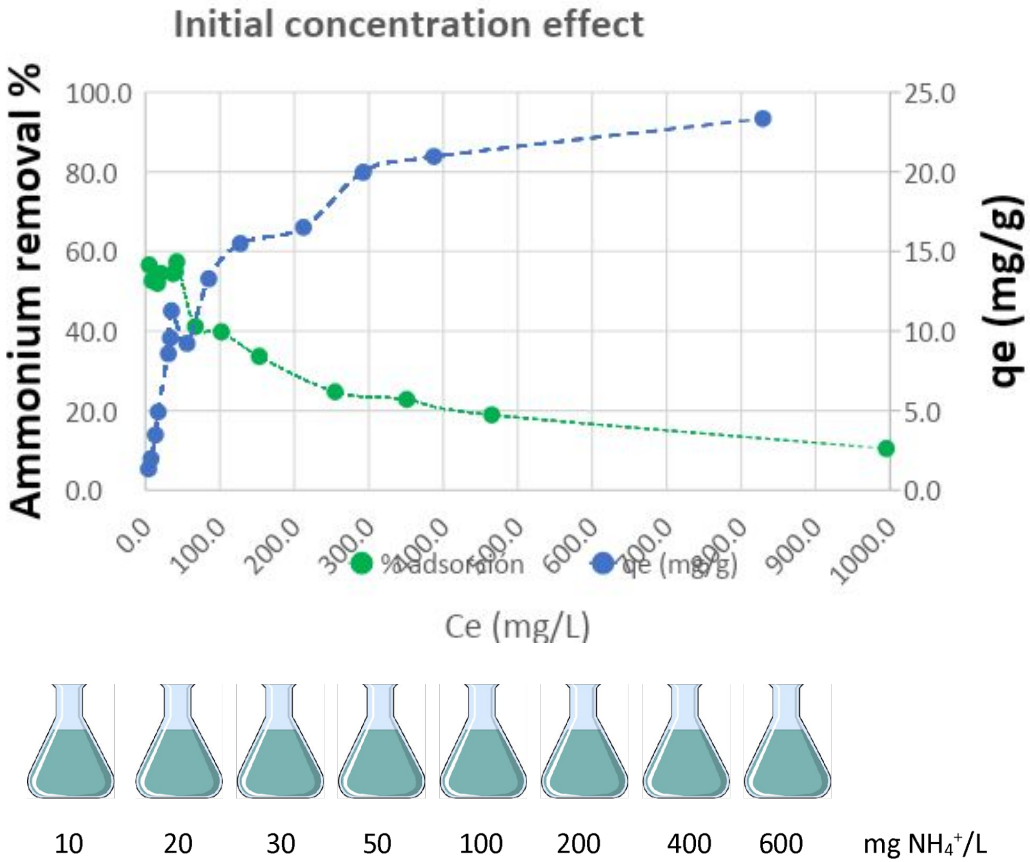


highest removal=5g/L

Batch tests



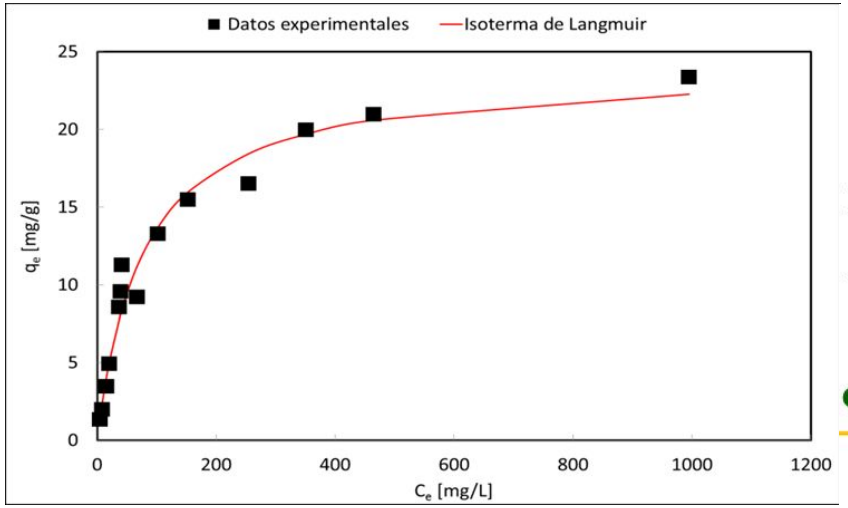
maximum adsorption=1h

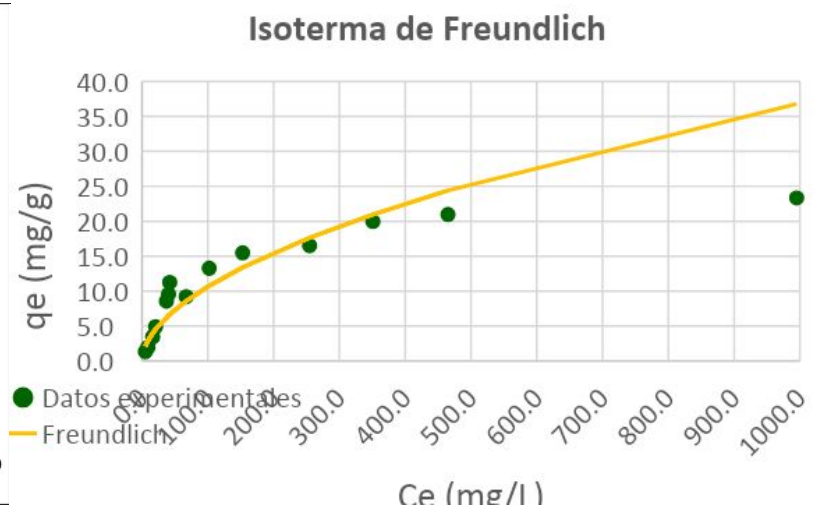


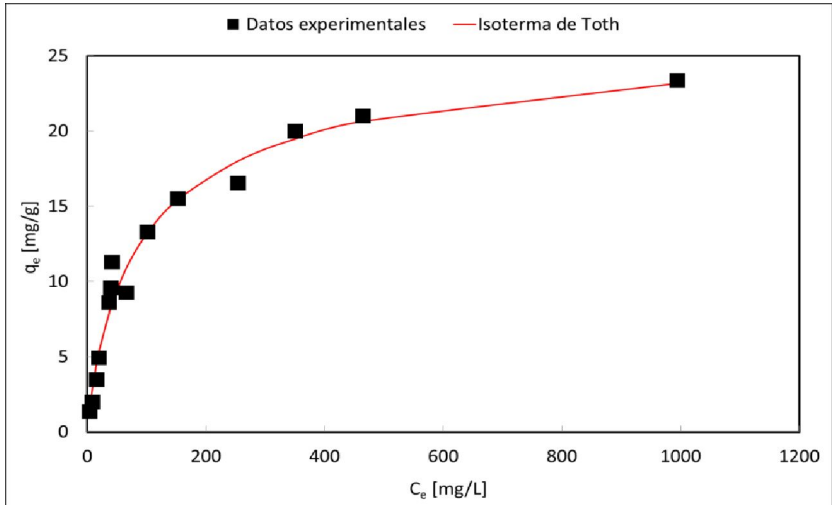
adsorbent capacity (q_e) = 23mg/g

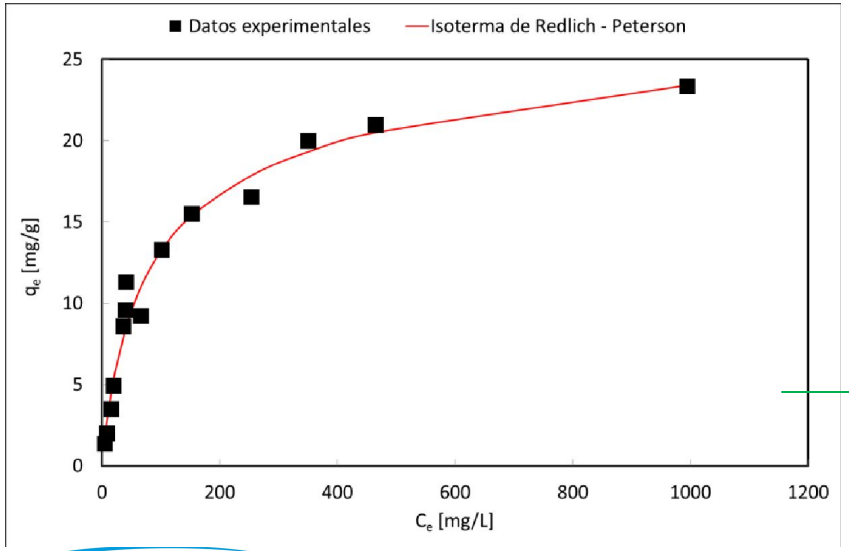
Isotherm study

Predict adsorption at a fixed T





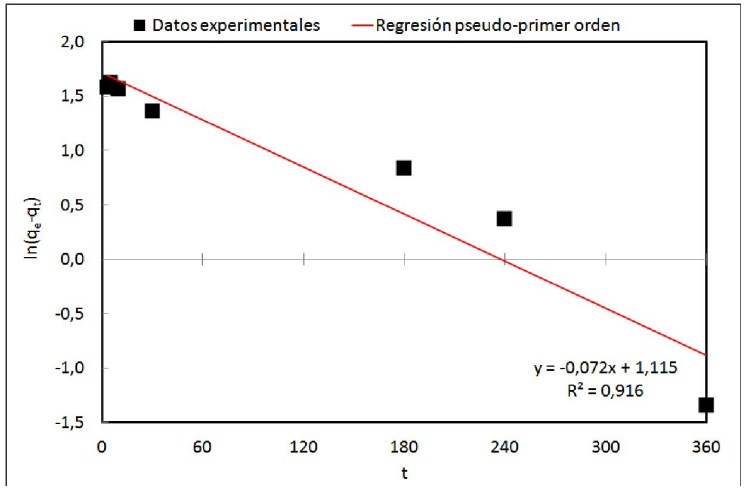


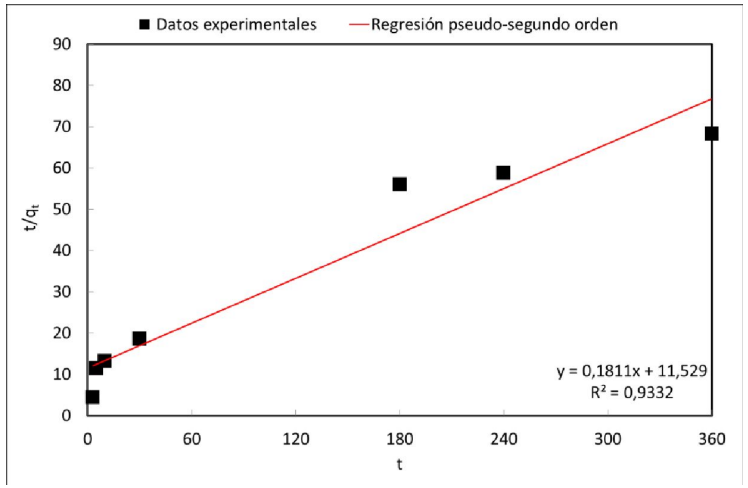


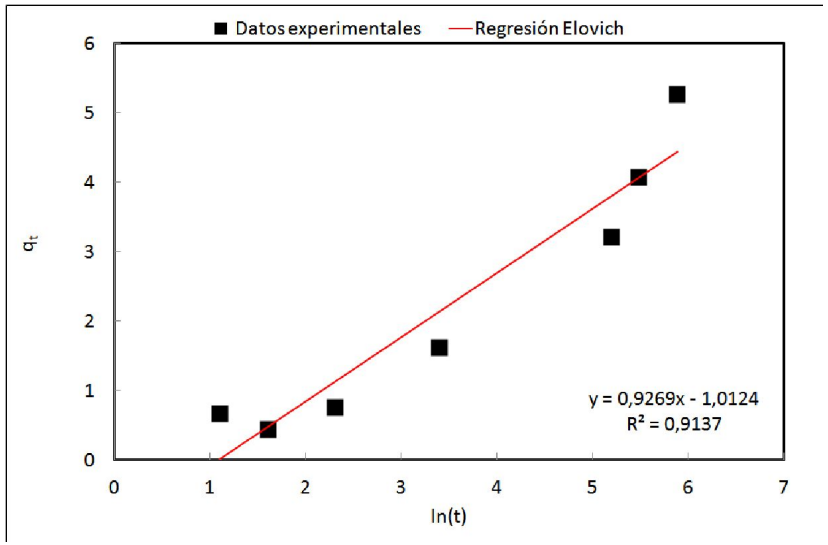
→ Redlich-Peterson

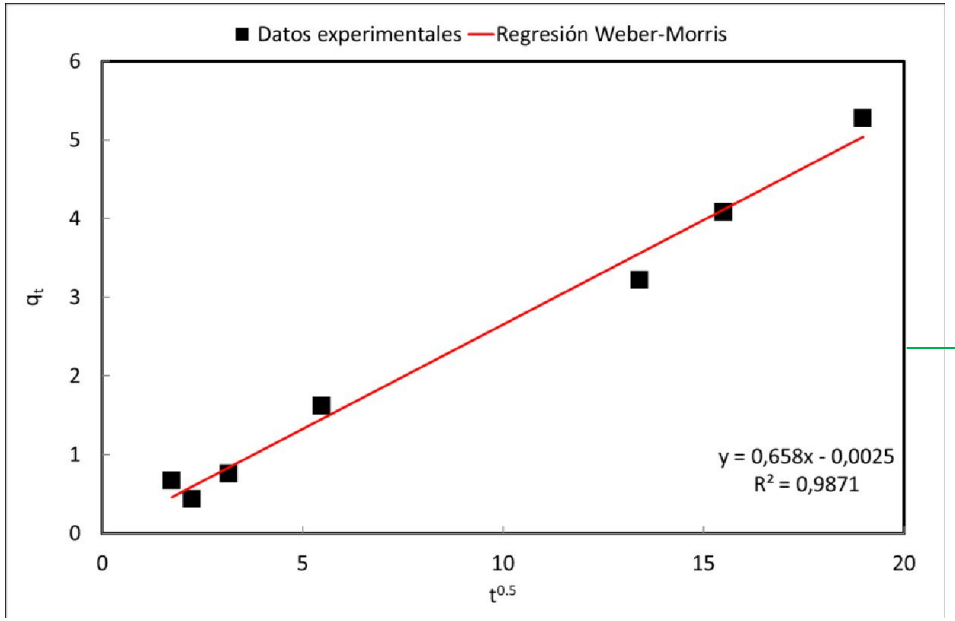
Isoterma	Langmuir	Freundlich	Redlich-Peterson	Tóth
RMSE	1,201	1,980	1,096	1,119
R^2	0,970	0,920	0,975	0,974

Kinetic study







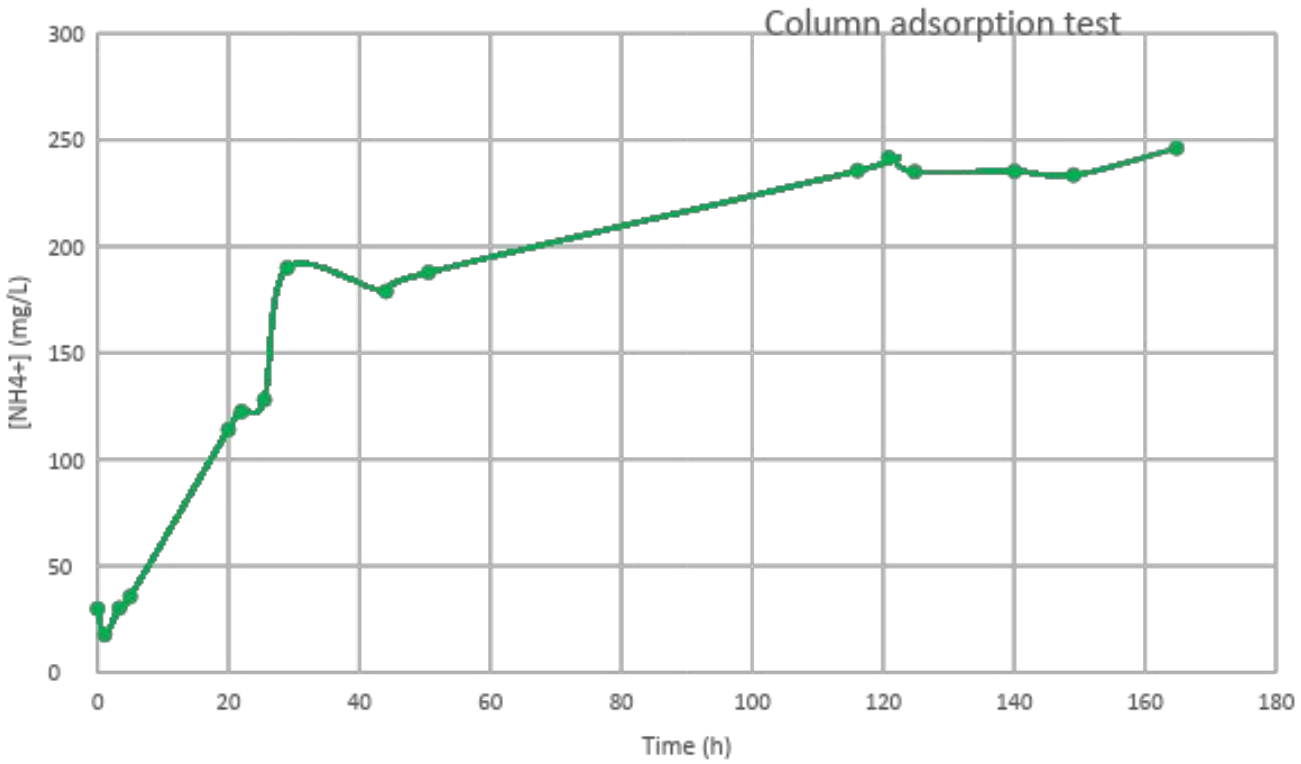


Weber-Morris

$$q_t = 0.2658 * t^{0.5} - 0,003$$

Continous tests

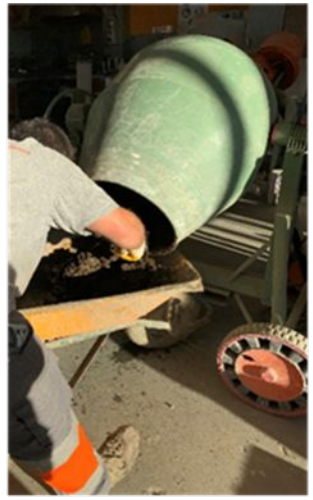
Parameter	Value
Grave size (mm)	4-8
Flow rate (mL/min)	6
Theorical NH_4^+ concentration (mg/L)	250
Real NH_4^+ concentration (mg/L)	248
Long test (h)	160



Maximum removal=short times
saturation=120h

Pilot plant

125L gravel form (4-12mm)
Crush and sieving.

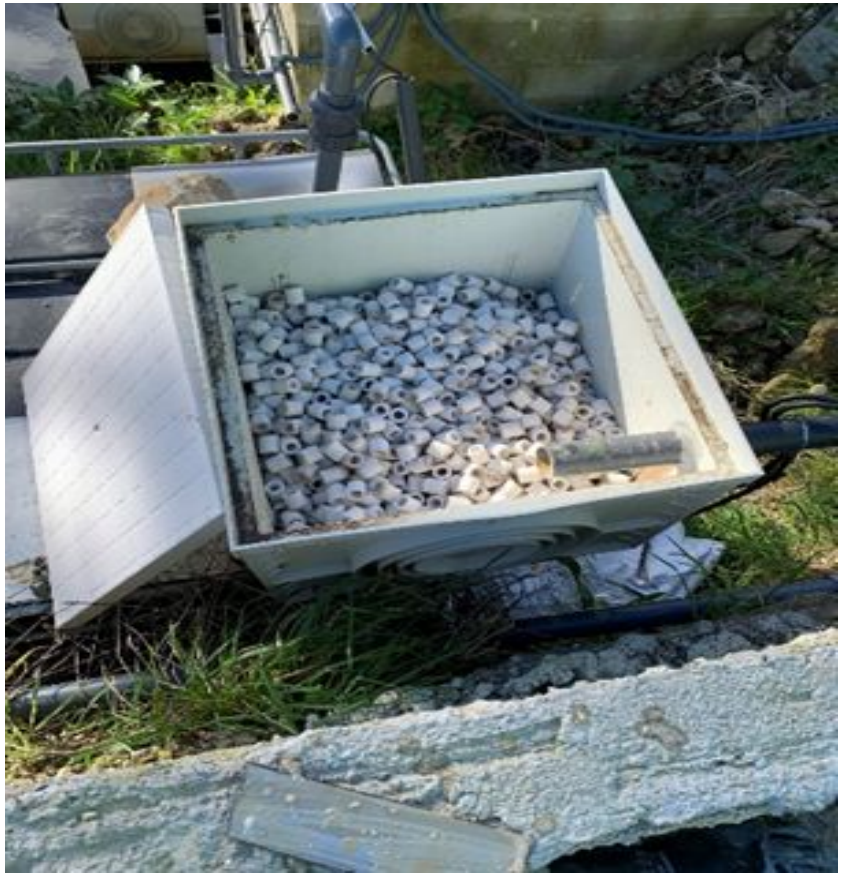


125L cylindric form (3cm diameter, 5 cm height)


Pilot plant
Xiloga landfill (wastewater treatment)

geopolymer gravel form in a wetland (125L)

Geopolymer cylindric form in a sump (125)



Adsorption results

	Leachate	Sump outlet (cylindres)	Wetland outlet (grave)
pH	8,4	11,6	13,3
EC (mS/cm)	22,5	11,7	60,4
Amonio (mg/L)	91	59	17

High ammonium removal.
Over 80%

High electrical conductivity
High alkalinity

Conclusions

- ❑ High ammonium removal, over 80%. Slightly superior to zeolites.
- ❑ Sustainable material.
- ❑ Low cost.
- ❑ Low operational costs.

- ❑ <u>Future works:</u>
  - ❖ Techniques/treatments to reduce the alkalis leaching.
  - ❖ Decrease the saturation time
  - ❖ Treatments to reuse adsorbents in different cycles.
  - ❖ Innovative designs to maximize adsorption: 3d printing
  - ❖ Test other contaminants: heavy metals, dyes, antibiotics...

Miguel Otero Sáenz de Lubiano miguel.otero@aimen.es
+34 98634400 Ext. 3210

Lorena Freire Piñeiro lorena.freire@aimen.es
+34 98634400 Ext. 3210

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¡MUCHAS GRACIAS!

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