

Responsible reduction of nitrates in the comprehensive water cycle



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As part of the project LIFE LIBERNITRATE (www.lifelibernitrate.com), financed by the European Union (EU), a sustainable circular economy process based on the valorisation of rice straw ashes for reducing nitrate in the integral water cycle are performed (Moliner *et al.*, 2018). Awareness was also raised amongst farmers of the environmental impact of the excessive use of nitrogen.

The project has used rice straw as a source of silica to develop an adsorbent, which was patented (Primaz *et al.*, 2021). A green silica modification was carried out by using APTES to obtain an amino-functionalised silica adsorbent. The goal of this strategy was two-fold: reduce the negative effects of burning straw rice in the field, and use the modified silica to reduce nitrate content in waters.

Silica synthesis

Experiences during the project demonstrated that silica synthesis at the lab is scalable by a factor of around 500. The adsorption capacity was checked with that obtained by a commercial resin, providing improved results. The synthesis method at a large scale was compared with traditional industrial methods and green adsorbents. It can be concluded that this is a green process that reduces solvent consumption, time, and it does not require high temperatures (Robles-Jimarez *et al.*, 2022).

Prototypes

The active silica is used in a pilot project developed in a drinking water treatment plant. It consists of the reduction of 30 per cent of the nitrate concentration from the integral water cycle. Well water and wastewater from an osmosis plant

are studied. Several prototypes have been developed within the framework of the project:

- An own-designed incineration plant. The unit's design is highly bespoke, considering the main quantitative objectives and the potential technical difficulties.
- A prototype to produce active silica from the controlled incineration of rice straw to obtain silica-rich ash.
- Several prototypes of the preparation and implementation of active silica beds to reduce the concentration of nitrates in the water cycle by acting: (a) in the water collector (from groundwater) and the reject water of an osmosis plant; and (b) in water from wells for human consumption in small municipalities to reduce the concentration of nitrates below 50ppm, without the use of an osmosis plant.



Figure 1: (a) incineration plant; (b) extraction and functionalisation reactor; (c) prototypes of silica beds.

Figure 1 shows (a) the incineration plant comprises four elements: storage, conveyor belt, incineration unit and gas treatment section, (b) extraction and functionalisation reactor, and (c) prototypes of silica.

Several controls are used in the different elements of the plant: (i) temperature controllers—inlet air, combustion chamber, outlet gas, ash container; (ii) feeding inlet flow and belt velocity; and (iii) volumetric flow—inlet air and outlet gas. All these variables are monitored through a controller that can work automatically following defined working conditions. All the system elements follow a fail-safe criterion to ensure they remain in the most secure form in case of failure.

Pellets enter the combustion chamber from the dosing silo through the feeding tube regulated by a rotary valve (Moliner, Bove and Arato, 2020). Air is conveyed from the outside into the combustion chamber through an air conveyor. Inside this chamber, on its back surface, two ignition glow plugs (250W each) are installed (length = 140mm). Downstream the combustion chamber, a smoke fan is installed with a dual function: (i) to extract the fumes from the combustion chamber towards the outside; and (ii) to ensure air entry. A box (length = 0.19m; width = 0.304m; height = 0.094m, for a total volume = 0.0055m³) is placed at the chamber's bottom to collect the ashes produced during combustion. The

chamber is closed with an isolated door with a glass window to observe the flame and visually control the process. Four temperature sensors are placed inside the chamber (top, gas outlet, hearth of the combustion chamber and ashes collector) whose measures are registered in the controller.

Demonstration and testing

Throughout the project, demonstration and testing tasks of the active silica beds, for the retention of nitrates in the water treatment plant of the Alginet municipality, have taken place. This includes verification of the correct operation on artisan manufacturing equipment, with different beds of gravel/silica, glass and Teflon. We worked on them with different configurations, in series and parallel, working two or more filters with these configurations and individually on each prototype. This first prototype allowed, by design, to observe the behaviour of the water when it came into contact with the silica-gel, to observe the behaviour of the flow of the fluid inside it, so that, throughout various tests, it was possible to optimise flow rates, and work pressures.

Other prototypes used fibre bottles, the type used in ion exchange. This industrialised equipment allowed work with higher flow rates and pressures, having a more stable behaviour with

different working modes. Likewise, the fluid inlet and outlet system ensures a greater permanence of the silica-gel within the container itself, reducing turbidity to values that allow continuous measurement with nitrate measurement equipment. At this point, the system is partially automated. Right now, it is not necessary to disconnect and/or connect pipes to exchange the processes of activation of the silica-gel or denitrification of the water. The flow can be directed towards the desired process via an electrical panel that controls various selectors and a series of solenoid valves.

With the application of existing adaptation systems on the market, industrialisation and implementation are facilitated, leaving some fringes such as a higher level of process automation, reducing the time required to change spent silica-gel, reducing trigger times etc., still in process.

Actions

During the four years of implementation of the LIBERNITRATE project and within the sub-action dedicated to raising farmers' awareness of the environmental impact of the excessive use of nitrogen fertilisers, the following actions have been carried out:

1. Fertilisation of three plots dedicated to the cultivation of persimmon, citrus,

and rice with slow-release fertilisers. The results show a reduction in the consumption of nitrogen fertilisers of more than 20 per cent with no reduction in production.

2. Development of an online self-training course on responsible fertilisation in nitrate vulnerable areas. This course aims to overcome the general lack of knowledge about this problem in the agricultural community and highlight the importance that reducing nitrogen fertilisation will have in practice after the new EU Common Agricultural Policy.

This course is divided into six modules in video format in Spanish, Italian and English (with subtitles in other languages), which can be watched independently. It is available on the project's Youtube channel.

The course modules are:

1. Fertilisation: basic notions
2. The Nitrates Directive and Vulnerable Zones
3. Nitrogen determination in soil
4. The New Common Agricultural Policy: good agricultural practices
5. The fertilisation programme
6. Practical cases of responsible fertilisation: the LIBERNITRATE project.

Impact measurement

Finally, the key indicator to measure the project's socio-economic impact

is the number of potential replicas. This information is relevant due to its influence on the number of inhabitants benefited, the jobs created, the presence of economies of scale and, in short, the viability of the project itself. Health indicators have also been identified as socio-economic aspects related to the project.

Prioritisation criteria have been established to implement the project in those areas with the greatest potential for generating social, economic and health benefits. These potential benefits will be greatest in areas where nitrate problems are most serious, and the barriers to reaching a solution are greatest. Those situations with a higher cost of non-action should have the highest intervention priority. This cost of inaction represents a key indicator when prioritising actions and determining the benefits derived from them. When the cost of implementing the project is much lower than the cost of not acting, we will have the guarantee of obtaining a favourable socio-economic impact. Monetary valuation methods have been proposed to quantify the cost of not acting or, equivalently, the benefits of acting.

According to the results obtained, the LIBERNITRATE project will be feasible through scalability. Scalability will increase the project competitiveness and will reduce unit production costs, facilitating large-scale implementation.

References

- Moliner, C., Teruel-Juanes, R., Primaz, C., Badia, J., Bosio, B., Campins-Falcó, P., Molins-Legua, C., Hernandez, F., Sanjuan-Navarro, L., Madramany, P., Morán, J., Castro, J., Sanchis, F., Martínez, J., Hiddink, F., Ribes-Greus, A. and Arato, E. (2018) 'Reduction of Nitrates in Waste Water through the Valorization of Rice Straw: LIFE LIBERNITRATE Project', *Sustainability*, 10(9), 3007. doi: 10.3390/su10093007.
- Moliner, C., Bove, D. and Arato, E. (2020) 'Co-Incineration of Rice Straw-Wood Pellets: A Sustainable Strategy for the Valorisation of Rice Waste', *Energies*, 13(21), 5750. doi: 10.3390/en13215750.
- Primaz, C.T., Jornet-Martínez, N., Sanjuan-Navarro, L., Moliner-Estopiñan, C., Campins-Falcó, P., Molins-Legua, C., Ribes-Greus, M.D., Badia-Valiente, J.D., Teruel-Juanes, R., Gil-Castell, O., Bosio, B. and Arato, E. (2021) *Procedimiento de adsorción de nitratos mediante sílica modificada activa a partir de ceniza de paja de arroz*. Spanish Patents and Trade Mark Office Patent no. E2727673 B2.
- Robles-Jimarez, H.R., Sanjuan-Navarro, L., Jornet-Martínez, N., Primaz, C.T., Teruel-Juanes, R., Molins-Legua, C., Ribes-Greus, A. and Campins-Falcó, P. (2022) 'New silica based adsorbent material from rice straw and its in-flow application to nitrate reduction in waters: Process sustainability and scale-up possibilities', *Science of Total Environment*, 805, 150317. doi: 10.1016/j.scitotenv.2021.150

PROJECT NAME

Life Libernitrate

PROJECT SUMMARY

LIFE LIBERNITRATE: responsible reduction of nitrates in the comprehensive water cycle.

PROJECT LEAD

AVSA is a private company specialised in the management of the integral water cycle.

DIVAL is a public entity that represents the 266 municipalities of the province of Valencia.

LWI is a business incubator that promotes incubation specifically for water technology.

UNIGE is a public university that participates through its DICCA research groups.

UNIO is a professional agricultural association that represents the farmers and ranchers of the Valencian Community.

UPV is a public university that participates through its DREMAP research groups.

UVEG is a public university that participates through its MINTOTA and ECON research groups.

PROJECT PARTNERS

A total of eight public-private entities form the consortium that develops the LIFE LIBERNITRATE project: Consorci de la Ribera (CRIB), Aguas de Valencia SA (AVSA), Provincial Council of Valencia (DIVAL), Stichting Incubator (LWI), Università degli Studi di Genova (UNIGE), La Unió de Llaoradors i Ramaders del País Valencià (UNIO), Polytechnic University of Valencia (UPV) and University of Valencia (UVEG).

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