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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 aminofunctionalised 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

during Experiences 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 50 ppm, 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 = 140 mm). 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 = 0.19 m; width = 0.304 m; height = 0.094 m, for a total volume = 0.0055 m<sup>3</sup>) 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.

 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
- The Nitrates Directive and Vulnerable Zones
- 3. Nitrogen determination in soil
- 4. The New Common Agricultural Policy: good agricultural practices
- 5. The fertilisation programme
- 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.

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### 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 represent the 266 municipalities of the province of Valencia.

LWI is a business incubator that promotes incubation specifically forwater technology

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

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

UPV is a public university that participate 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 Llauradors i Ramaders del Paísd Valencia (UNIO), Polytechnic University of Valencia (UPV) and University of Valencia (UVEG).

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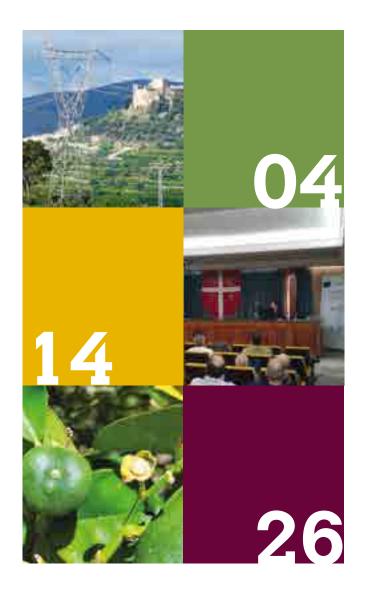
### Sumari

Entrevista a
Javier Viciano,
profesor de Derecho
Mercantil de la UV

LA UNIÓ aposta per les energies renovables, però amb un model ordenat i sostenible

LA UNIÓ pide que no se recorte ni un solo hectómetro cúbico de agua del trasvase Tajo-Segura





#### **ACTUALITAT**

**MODELO ENERGÉTICO** LA UNIÓ apuesta por las energías renovables de forma ordenada y sostenible, sin destrozar terrenos productivos y el paisaje rural **(04)** 

#### ENTREVISTA AMB...

**JAVIER VICIANO** profesor de Derecho Mercantil de la Universitat de València (07 i 08)

#### ELS PROJECTES DE LA UNIÓ

LIBERNITRATE Somos parte de la solución (14)

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### El proyecto Libernitrate: somos parte de la solución

I proyecto Libernitrate es otro de los proyectos LIFE en los que LA UNIÓ de Llauradors i Ramaders participa como socio, en este caso junto con el Consorcio de la Ribera, que es el líder del proyecto, las Universidades de Génova, de València y la Universitat Politècnica de València, la Diputación de Valencia, Global Ómnium SA (Aguas de Valencia) y Stichting Ingubator de Paises Bajos. / PEPE CASTRO

El objetivo del proyecto, iniciado en 2017, es reducir la concentración de nitratos en las plantas de osmosis inversa que suministran agua potable a las poblaciones situadas en Zonas Vulnerables mediante el desarrollo y uso de una tecnología muy innovadora y de enorme proyección de futuro, una sílice activada proveniente de la quema controlada, en caldera, de la paja del arroz.

Ese objetivo se enmarca en una visión global del ciclo del agua, y, por supuesto, LA UNIÓ desde el principio aposto por él. Es indudable que el sector agrícola es parte de la solución para paliar la contaminación de los recursos hídricos. Ese ha sido precisamente nuestro papel en este proyecto, demostrar que con el adecuado asesoramiento podemos mejorar entre todos el impacto contaminante por nitratos.

Durante dos años, hemos demostrado en cultivos de caqui, cítricos y arroz que utilizando abonos de liberación lenta pueden obtenerse rendimientos muy similares o mejores a los obtenidos utilizando fertilizantes convencionales, pero con una reducción de consumos que ronda y, en algunos casos, supera con mucho, el 20%. No podemos decir que sea una evidencia científica, no lo es, porque serían necesarias muchas más pruebas y ensayos especialmente dirigidos por instituciones científicas, pero al menos hemos abierto, nosotros los agricultores, una ventana a esos ensayos.

Somos conscientes que esos fertilizantes de liberación lenta no son la única solución, la agricultura de conservación y la agricultura de precisión van a tener un papel muy importante para reducir y hasta eliminar el exceso de nitratos. También estamos trabajando en estas líneas y seguiremos informando cuando tengamos más soluciones.

Durante el confinamiento, hemos reflexionado mucho acerca de este proyecto, ¿cómo expandir la experiencia?, ¿cómo ayudar a nuestras Administraciones Públicas y a la población en





general?, ¿cómo contribuir a la mejora de nuestros recursos hídricos desde el sector?

La respuesta es un curso de formación online, autoformativo, que estamos a punto de finalizar. Un curso innovador, dividido en módulos, en el que cada agricultor pueda tener información de la situación de la agricultura en las zonas vulnerables por nitratos y más aún ahora cuando los nuevos eco-esquemas de la PAC inciden decididamente en esta situación ambiental.

Obviamente este curso no puede cambiar drásticamente las maneras de trabajar, pero sí al menos dar información veraz sobre qué hacer, y eso es lo primero y más importante, es práctico. Queremos destacar además que los filtros de sílice activada funcionan y más de lo que esperábamos, los resultados de retención (y no sólo de nitratos) son impresionantes. No está muy lejano el día en el que, posiblemente, la paja de arroz se convierta en la solución para dar de beber con calidad a multitud de pequeños pueblos sin plantas de osmosis con las que reducir los nitratos en su agua potable. Una perspectiva social y de apuesta por el desarrollo rural que es, para nosotros, un deber con nuestros conciudadanos.

http://www.lifelibernitrate.com/







Article

### Reduction of Nitrates in Waste Water through the Valorization of Rice Straw: LIFE LIBERNITRATE Project

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Abstract: An improved and more sustainable waste management system is required for successful development of technologies based on renewable sources. Rice straw is submitted to controlled combustion reactions and the produced ashes are chemically treated to produce silica. After a chemical activation step, the activated silica shows potential as an adsorbent agent and will be used to remove the excess of nitrates in groundwater and wells in the area of Alginet (Valencia, Spain), selected as a vulnerable zone within the Nitrates Directive. The demonstration activity aims to have a local impact on municipalities of 200 inhabitants or fewer, decreasing from current nitrate concentrations close to 50 mg/L, to a target of 25 mg/L. In a successive step, the methodology will be transferred to other municipalities with similar nitrate problems (Piemonte, Italy) and replicated to remove different pollutants such as manure (the Netherlands) and waste waters from the textile industry (Italy).

**Keywords:** rice straw; waste management; energy and material recovery; water treatment; nitrate removal

### 1. Framework of LIFE LIBERNITRATE Project

Clean water is becoming a valuable commodity. In the last one hundred years, water consumption per capita has increased twice as fast as the population, with this trend expected to increase in the coming decades [1]. This can be attributed to increased water consumption and waste, irregular water distribution worldwide, climate change and the growing number of anthropogenic activities [2].

Sustainability **2018**, *10*, 3007

Efficient resource use plays a key role in activating economic agents, ensuring a social welfare state and life quality. The development of new strategies for resource supply and for promoting new markets must be paramount in policies all over the European Union.

In the past, several measures aimed to improve environmental quality have been adopted by the European Union (EU). As far as water is concerned, a Water Framework Directive [3] has been approved to establish clear criteria for evaluating the chemical status of water and for identifying and reversing trends in the deterioration of its quality. The application of these criteria [4] has had a high impact on global water conservation over the last decade, which may have led to reduced water consumption. Now, a focus on improving water quality is necessary to achieve significant and long-lasting water savings [5].

Sources of production, use and disposal of numerous chemicals employed in medicine, industry, and even common household conveniences have led to the widespread occurrence of organic pollutants in water [2]. Among them, agricultural activities are a source of elevated concentration of contaminants [6–9]. The use of chemical fertilizers has increased from 14 million tons in 1954 to a predicted 200 million tons in 2018 [10]. Nitrogen fertilizers trigger harmful environmental processes, such as eutrophication [11], acidification [12], water pollution [13,14] and emission of nitrogen oxides (NOx) [15]. Nitrogen compounds in surface and groundwater become a health risk for animals [16] and for humans when polluted water is used to produce drinking water [17]. In humans, nitrate is reduced to nitrite that converts hemoglobin to methemoglobin, and is unable to transport oxygen [18].

In Europe, 87% of groundwater contains excess nitrates [19]. In intensive farming and cattle-rearing areas, nitrate concentration in groundwater can reach up to seven times the legal limit. The number of areas vulnerable to this pollution has increased, especially in Spain, Germany, the UK, Denmark and the Netherlands, among others, according to the Nitrates Directive [20], an integral section of the Water Framework Directive [3].

In addition to water pollution, agricultural activities are also responsible for a large quantity of waste that needs to be dealt with. Rice straw, for example, is usually eliminated by uncontrolled burning with harmful consequences related to air, flora and fauna pollution in wetlands. Currently, different European moratoria permitting uncontrolled burning are being applied, since no liable Before that, rice waste was abandoned or sunk, thus, solutions are being implemented. being decomposed in fields, causing major die-off of fish and other aquatic fauna in deeper areas [21]. As a sustainable alternative, the reliability of agricultural by-products as precursors of materials with high adsorptive capacities has been demonstrated recently [22]. Adsorption is considered among the best methods for the removal of water pollutants due to its ease of operation and the ability to remove different types of pollutants, giving it a wider applicability in water quality control [23]. In particular, rice waste stands out as a good precursor of adsorbent materials for the removal of metals such as, Pb (II) and Hg [24], Cd (II) [25] among others. In addition, Orlando et al. achieved a maximum adsorption capacity for nitrate from rice hull with values of 1.21 mmol/g [26]. Moreover, rice waste ashes possess a composition with high silica content that, after an activation step, can be used in the removal of inorganic and organic pollutants from aqueous solutions [27].

In this framework, the present work describes the production of silica-based adsorbents obtained from the controlled combustion of rice straw and the preliminary lab scale tests on their use in nitrate removal from contaminated waters. The results demonstrate the suitability of the proposed methodology and identify potential improvements for the process.

The implementation of this methodology is described successively through the main actions and expected outcomes of the EU-funded project LIFE LIBERNITRATE [28]. In general, it aims to be a synergic application of efficient rice waste management, at a local level, to treat nitrate problems in overcropping areas. This way, initially considered (hazardous) waste is turned into new resources, completing a re-use cycle and promoting zero-waste scenario policies.

Sustainability **2018**, *10*, 3007

### 2. Context and Technological Background

Rice is one of the most consumed crops worldwide, with an annual production of 700 million tons according to the Food and Agriculture Organization of the United Nations database [29]. Italy and Spain account for 80% of the European rice production: Italy is the leading European producer with a total cultivated surface of 220,000 ha. The crop is primarily grown in the Po basin (the Piedmont, Lombardy, Venetia, and the Romagna). The second largest European rice producer is Spain, with 117,000 ha. Andalucia and Valencia are the main rice-producing regions, the latter harboring a more stable water supply which benefits the production.

In order to establish sustainable management of rice harvest residues in the major producing areas that is transferrable to other communities with identical problems, the methodology shown in Figure 1 is proposed. It consists of an initial pretreatment and densification of rice straw (Section 2.1) to optimize the subsequent energy valorization (Section 2.2). Afterwards, the obtained ashes are submitted to a material valorization (Section 2.3) and the products are used for water treatment (Section 2.4) which completes the re-use cycle. A complete description of the mentioned sub-sections is described in the following paragraphs.

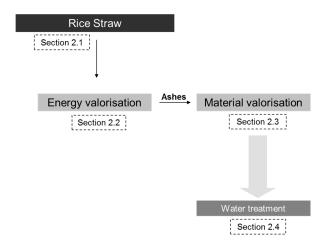
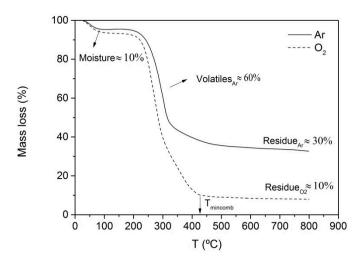


Figure 1. Proposed methodology for sustainable management of rice straw.

### 2.1. Characterization and Pre-Treatment of Rice Straw

Rice straw (RS) can be described in terms of its chemical properties through its ultimate (UA) and proximate analysis (PA) and its energy content (HHV) [21,30]. Thermogravimetric analysis (TGA) was applied to assess the thermal decomposition profiles as previously described for persimmon [31], apple tree residues [32] or biopolymers [33]. Experiments were carried out in a Mettler Toledo TGA/SDTA 851 (Columbus, OH, USA). Samples weighing about 5 mg were heated in an alumina holder with a capacity of 70  $\mu$ L. Experiments were performed from 25 °C to 800 °C at 2 °C/min under a constant flow of 50 mL/min of gas for analysis. Figure 2 shows the thermogravimetric curves (TG) at 2 °C/min under inert (full line) and oxidative (dashed line) conditions.

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**Figure 2.** Thermogravimetric analysis (TGA) decomposition of rice straw (RS) at 2 °C/min at inert (full line) and oxidative (dashed line) conditions.

In short, TG curves first displayed a degradation profile corresponding to the removal of moisture followed by the release of volatiles. Ashes could be calculated as the difference between the residues in both atmospheres (%ashes  $\approx$  20%) in accordance to previous analysis [21]. Overall, the good agreement with previously calculated compositions could confirm the suitability of TGA to obtain the proximate composition of biomass. RS was completely oxidized above  $T_{mincomb} \approx 430\,^{\circ}\text{C}$  and, accordingly, it was defined as the minimum furnace temperature to ensure its complete combustion.

The physical properties of RS are presented in Table 1. Its low bulk density is one of the major barriers in its effective utilization as a biofuel [34]. Compacting loose material to form a densified, homogeneous product improves its physical properties and results in easy feeding and handling. Initial compaction tests were performed using straw with dimensions  $5 \times 2 \times 1$  mm and a pelletizer with a maximum capacity of 200 kg/h working at 60–70 °C. No ligand was necessary as moisture was in the range 10–12% (see Figure 3).



Figure 3. Pellets of rice straw.

Finally, the energy content was evaluated obtaining a LHV<sub>RS</sub> = 10 MJ/kg, a much lower value with respect to the densified sample (LHV<sub>pellets</sub> = 15 MJ/kg [35]), confirming the suitability of the pre-treatment of RS from an energetic point of view as well.

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Table 1. Physical properties of RS and reference bulk density of pellets of RS.

ρ <sub>apparent</sub> (g/L)	ρ <sub>bulk</sub> (g/L)	ε (—)	ρ <sub>bulk-pellets</sub> (g/L) [36]
239	56	0.76	600

### 2.2. Energy Valorisation of Rice Straw

A feasibility study for the use of rice straw as an energy vector was performed with Aspen Plus<sup>®</sup>. An equilibrium model was used to simulate the combustion of 10 kg/day of RS that was introduced into Aspen Plus<sup>®</sup> as a non-conventional component defined by its proximate and ultimate analyses, together with its HHV [37]. In short, the model was composed by an initial decomposition step to transform the non-conventional component into compounds present in Aspen database [38]. Successively, a RGIBBS block simulates the combustion of the decomposed rice straw using air in stoichiometric conditions as the reaction agent. The temperature was set at a minimum value of 430 °C to ensure complete combustion and maximum ash yields.

As a result, an output of  $3.65~\mathrm{kW_{th}}$  and  $2~\mathrm{kg/day}$  of RS ash were theoretically obtained. Figure 4 shows the overall balance of the whole process for the given inlet conditions.

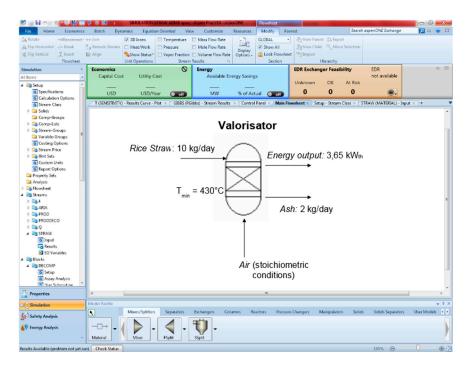
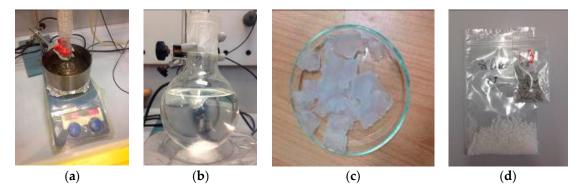


Figure 4. Overall balance of the valorization of RS.

### 2.3. Material Valorisation of Rice Straw Ash

Ashes from RS were obtained at lab scale through their controlled combustion in a muffle furnace. Ashes were chemically treated as fully described in Reference [39]. In short, the process involved an alkali dissolution (Figure 5a) followed by an acid precipitation of the product (Figure 5b). The obtained gel (Figure 5c) was then washed, dried and filtered to produce the final amorphous silica (Figure 5d).

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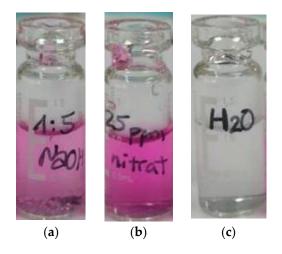


**Figure 5.** Alkali dissolution of rice straw (a); neutralization with sulfuric acid (b); silica gel (c) and silica powders (d).

### 2.4. Product Assessment

The application of silica for water treatment, in particular the removal of nitrates from water, is discussed. Water with a high content of nitrates was submitted to preliminary adsorption tests using the previous products. A total of 50 mg of an active silica sample was weighed and set in a cartridge (Figure 5a). Then, 0.5 mL of a 25 ppm  $NO_3^-$  solution was prepared as the initial solution (Figure 5b) that passed through the cartridges containing acidic silica.

Figure 6 presents the results of the preliminary tests. Figure 6a shows the initial nitrate solution after passing through cartridges containing acidic silica. Qualitatively, this solution presents a lighter colour, indicating a lower presence of nitrates in respect to the initial sample (Figure 6b). Quantitatively, a decrease of 30% in the nitrates concentration respect to the initial 25 ppm was achieved. Although pollutant retention was not complete (blank of water shown in Figure 6c), it might be sufficient to meet the legislation regarding waste waters in some cases.



**Figure 6.** Solution after passing through acidic silica (**a**); initial 25 ppm nitrate solution (**b**); blank of water (**c**).

To improve the efficiency of the process, the original silica samples were submitted to an activation step (procedure under patent review). Figure 7 shows the results achieved by processing, on line in a laboratory manifold, waste water of an osmosis plant at a flow rate of 11 mL/min for 5 min in a bed containing 2 g of active silica.

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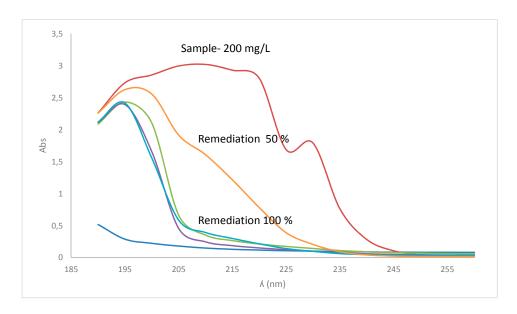


Figure 7. Remediation of nitrate achieved continuously.

From the technological background, it has been demonstrated that activated silica obtained from rice straw ash could be used in water treatment methodologies. This could be done as (1) a preliminary stage before conventional treatments in order to decrease the quantity of nitrates and decrease requirements of residence time and energy of the whole process or as (2) an alternative pathway if efficiencies are increased even avoiding the need for inverse osmosis plants.

In this framework, the EU-funded project LIFE LIBERNITRATE arises as a solution to treat waste waters using renewable residual sources.

### 3. LIFE LIBERNITRATE: Project Overview

The described methodology is the core of LIFE LIBERNITRATE. The main demonstration stage is carried out in Alginet (Valencia, Spain). This municipality has been selected as a vulnerable zone within the Nitrates Directive [20], with several wells currently abandoned or out of service as they do not meet the required quality standards to be considered as a source of drinkable water. The last public studies regarding water quality (2013) stated nitrate concentrations of 48 ppm, showing an increasing trend. The European Directive establishes that the maximum allowed concentration of nitrates cannot exceed 50 ppm, a value that is almost achieved, and, depending on the season of the year and the agricultural activities, can even be surpassed in some cases. For this reason, efficient techniques to recover existing wells and to guarantee good water quality have become necessary in the selected area of study. Additionally, the Natura 2000 national park of L'Albufera, located nearby Alginet (see location in Figure 8), is affected by this type of contamination, as the water's final destination is its lagoons.

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Figure 8. Geographical location of Alginet and L'Albufera.

The consortium of LIFE LIBERNITRATE (Figure 9) is composed of five technological partners (Universidad Politecnica de Valencia—UPV, Universidad de Valencia—UV, Università degli Studi di Genova—UNIGE, Aguas de Valencia—AVSA and Stichting Incubator—LWI) and three territorial partners (Consorci de la Ribera—CRIB, Uniò di Llauradors i ramaders—UNIO and Diputacion de Valencia—DIVAL).

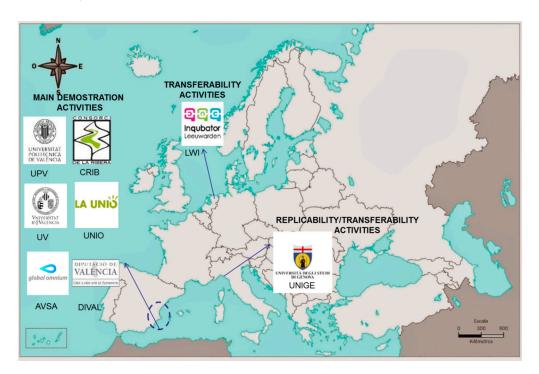


Figure 9. LIFE LIBERNITRATE consortium.

The main objective of the activities is to reduce the concentration of nitrates in the comprehensive water cycle by using an integrated and innovative approach based on the use of an adsorption bed made of active silica obtained from the controlled burning of rice straw ashes. The project started in October 2017 and will last three years. It is comprised of 16 interrelated tasks distributed in five categories: three preliminary actions (already finished), six implementation actions, three monitoring actions, two dissemination actions and two coordinating actions.

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The prototype to obtain controlled ashes from pelletized rice straw is currently under construction in Alginet (Spain). Its initial design, shown in Figure 10, was completed in May 2018 and its activity is expected to start in January 2019.

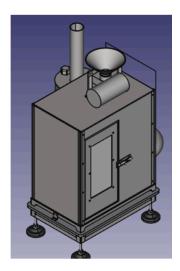


Figure 10. Initial design of the prototype to obtain rice straw ashes.

The activities in the water treatment plant using the prepared active silica beds will also start at the beginning of 2019. The targeted goals are:

- Direct purification of at least 26 m<sup>3</sup>/day of well water, reducing the nitrate concentration to at least 25 ppm. The prototype will be directly transferrable to municipalities of 200 inhabitants or fewer;
- An expected reduction of 90% in the concentration of nitrates in 130 L/day of water effluent in drinking water to facilitate compliance with the Nitrates Directive, and in the reject water of a reverse osmosis plant;

The methodology will be applied to a municipality in the area of Alginet, 24 km², and other municipalities of CRIB, with a total area of 1230 km². By demonstrating its feasibility and ensuring knowledge sharing and transparency, it will serve as a management system model to be replicated and extrapolated to the rice fields of the European Union. At the same time, this methodology will also be transferred to the treatment of water for the removal of other contaminating elements. In this context, replicability actions will be carried out in Piemonte (Italy) to treat water with high nitrate concentrations, whereas transferability actions will be aimed at the treatment of textile effluents (Italy) and manure (the Netherlands) during the third year of project implementation.

Finally, monitoring activities are being carried out during the whole implementation stage to assess the impact of the methodology on the environmental and socio-economic overall performances.

### 4. Conclusions

A methodology based on the sustainable management of rice straw has been defined. Firstly, its initial pretreatment and densification to optimize the subsequent energy valorization has been performed. Afterwards, the obtained ashes have been submitted to a material valorization obtaining silica with adsorbent properties that will be used for the removal of nitrates from contaminated waste waters. A 30% decrease in the nitrate concentration in respect to the initial 25 ppm was achieved. This method could be an initial pretreatment in current water technologies that would decrease the energy requirements of the process or, if efficiencies are further improved, it could even replace traditional osmosis plants. At the same time, this methodology can also be transferred to the treatment of different types of waste water, such as textile effluents or manure.

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**Author Contributions:** Writing-Original Draft Preparation, C.M.; Writing-Review & Editing, P.C.-F., A.R.-G.; Visualization: R.T.-J., C.T.P., J.D.B., B.B., C.M.-L., L.S.-N., F.H., J.M., J.C., F.J.S., J.D.M., F.H.; Supervision, E.A.; Project Administration, P.M.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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Review

## Modelling of Spouted and Spout-Fluid Beds: Key for Their Successful Scale Up

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Abstract: The development of robust mathematical models could provide the necessary tools for a more rapid, efficient, and reliable spouted bed technology development. Computer simulations can be very useful to aid this design and scale-up process: firstly, they can contribute to obtain a fundamental insight into their complex dynamic behavior by understanding the elementary physical principles such as drag, friction, dissipation etc.; secondly, the simulations can be used as a design tool where the ultimate goal is to have a numerical model with predictive capabilities for gas-particle flows at engineering scale. Clearly, one single simulation method will not be able to achieve this goal, but a hierarchy of methods modelling phenomena on different length and time scales can achieve this. The most fruitful approach will be when they are simultaneously followed, so that they can mutually benefit from each other. In this sense, this paper presents a review of the current state of the art of modelling on spouted and spout-fluid beds through an analysis of recent literature following a multiscale approach (molecular and particle, lab, plant and industrial scale). The main features of the different scales together with their current limits are discussed and specific topics are highlighted as paths that still need to be explored. In summary, the paper aims to define the theoretical setline and the basis of improvement that would lead to a robust multiscale model with solid links between micro and macroscopic phenomena. If done with the correct balance between accuracy and computational costs it will gear SB towards their reliable and successful implementation.

**Keywords:** spouted and spout-fluid bed; modelling; multiscale approach; scale-up; CFD; multiphase flows

### 1. Framework of the Experimental Applications of the Technology

Spouted and Spout-Fluid Beds (SB) have been object of intense research during the past decades. The terms spouting and spouted bed were given by [1] at the National Research Council (NRC) of Canada to describe an innovative device based on fluidization technologies. Gishler and Mathur described this technology as "a flowing mechanism for solids and gas different from fluidisation but it achieves the same purpose for coarse particles as fluidisation does for fine materials". In contrast with traditional fluidization [2], the fluid flow enters into the spouted bed through a single central inlet orifice creating three well differentiated zones: the central core of the reactor through which air flows is the spout, the surrounding annular region is the annulus and the solids above the bed surface entrained by the spout and going down the annulus form the so-called fountain. As an example, Figure 1 shows the different stages of spouting from the static bed situation (a) to a fully developed spouting regime (b) where the three previously mentioned zones can be easily identified.