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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].

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 solutions are being implemented. Before that, rice waste was abandoned or sunk, thus, 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.

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.

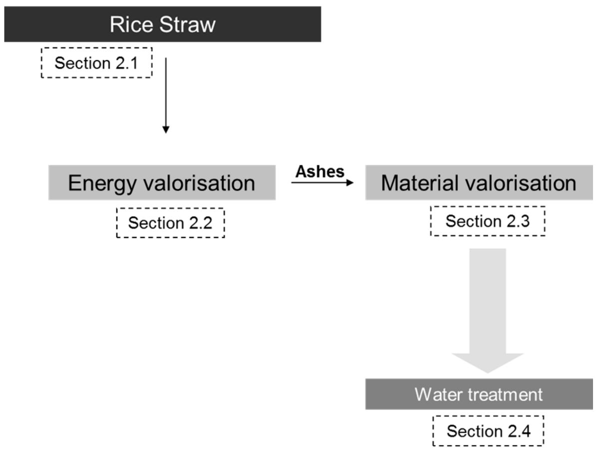


Figure 1. Proposed methodology for sustainable management of rice straw.

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 μL. 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.

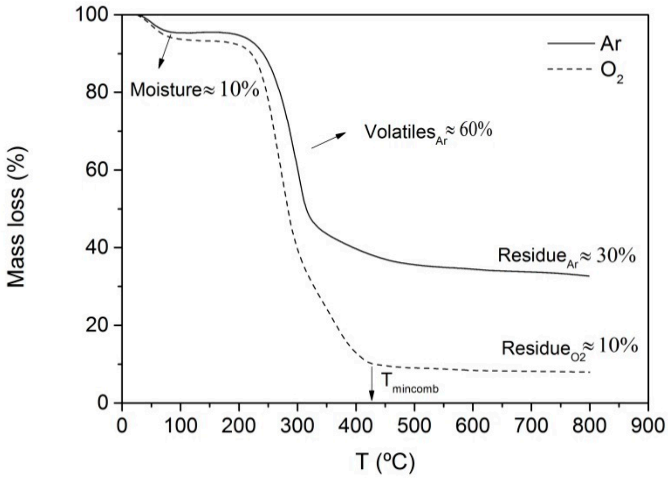


Figure 2. Thermogravimetric analysis (TGA) decomposition of rice straw (RS) at 2 °C/min at inert (full line) and oxidative (dashed line) conditions.

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 ≈ 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 $T_{mincomb} \approx 430$ °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 × 2 × 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_{RS} = 10 MJ/kg, a much lower value with respect to the densified sample ($LHV_{pellets}$ = 15 MJ/kg [35]), confirming the suitability of the pre-treatment of RS from an energetic point of view as well.

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

$\rho_{apparent}$ (g/L)	ρ_{bulk} (g/L)	ε (−)	$\rho_{bulk\text{-}pellets}$ (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®. An equilibrium model was used to simulate the combustion of 10 kg/day of RS that was introduced into Aspen Plus® 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 kW_{th} and 2 kg/day of RS ash were theoretically obtained. Figure 4 shows the overall balance of the whole process for the given inlet conditions.

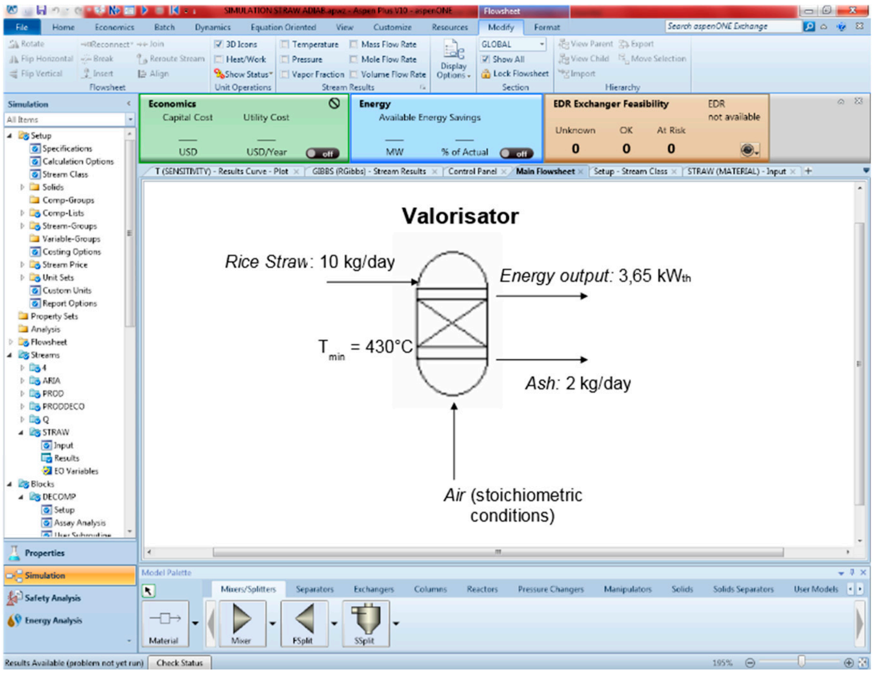
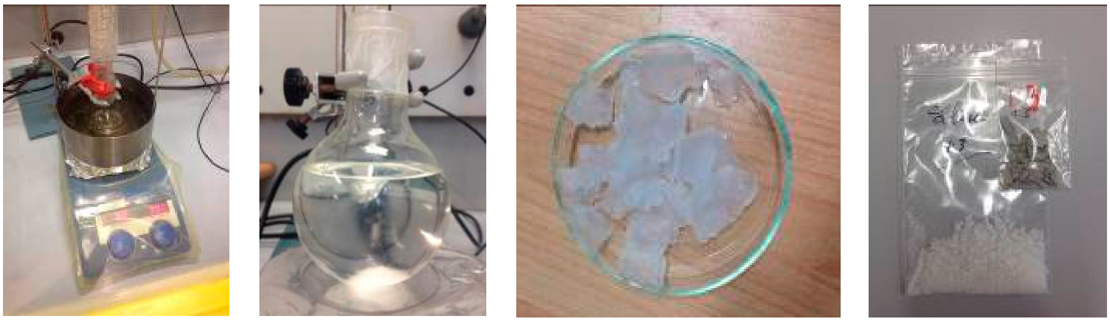


Figure 4. Overall balance of the valorization of RS.

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).



(a) (b) (c) (d)

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.

(a) (b) (c)

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.

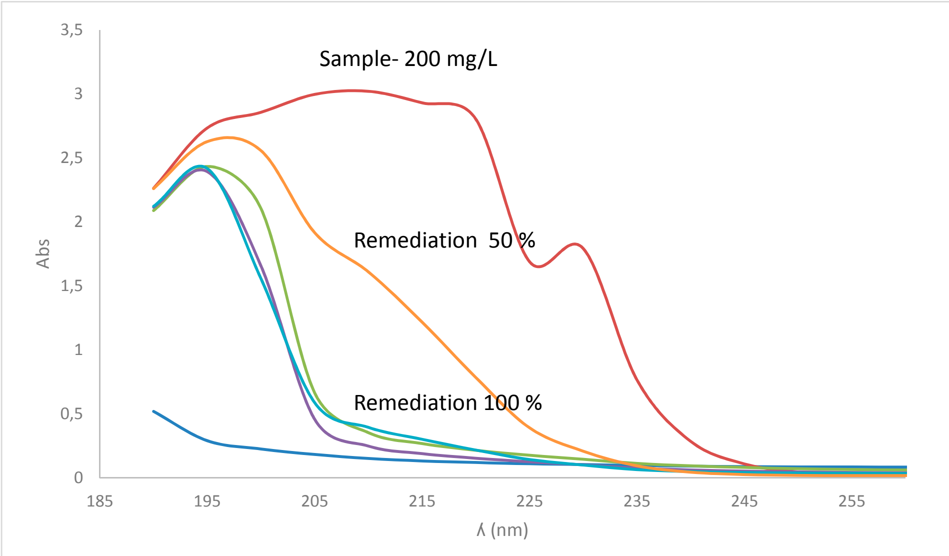


Figure 7. Remediation of nitrate achieved continuously.

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.

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).

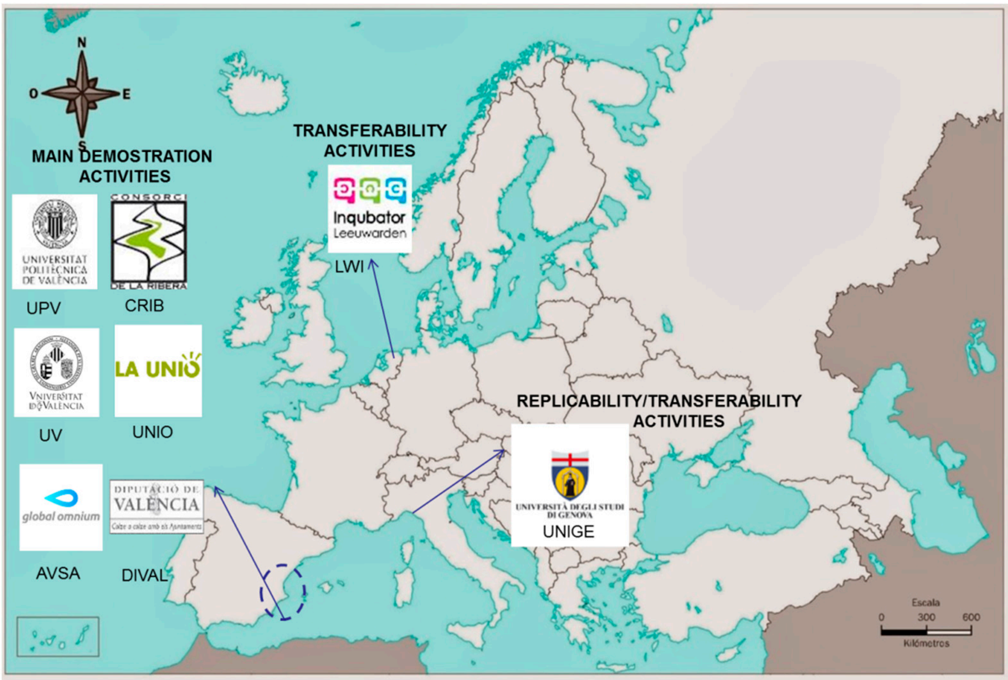


Figure 9. LIFE LIBERNITRATE consortium.

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.

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.

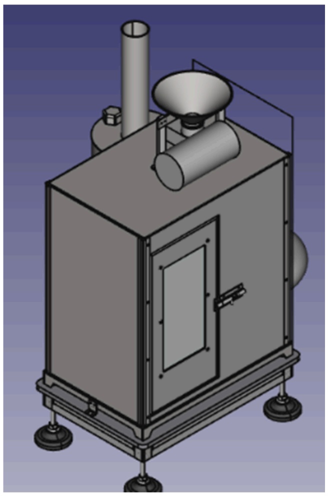


Figure 10. Initial design of the prototype to obtain rice straw ashes.

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^3/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 km^2, and other municipalities of CRIB, with a total area of 1230 km^2. 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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