



New silica based adsorbent material from rice straw and its in-flow application to nitrate reduction in waters: Process sustainability and scale-up possibilities

H.R. Robles-Jimarez^a, L. Sanjuan-Navarro^a, N. Jornet-Martínez^a, C.T. Primaz^b, R. Teruel-Juanes^b, C. Molins-Lagua^a, A. Ribes-Greus^b, P. Campíns-Falcó^{a,*}

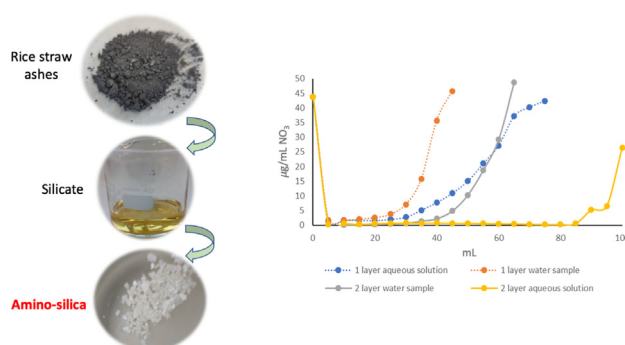
^a MINTOTA Research Group, Departamento de Química Analítica, Facultad de Química, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

^b Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València, 46022, Valencia, Spain

HIGHLIGHTS

- Valorization of rice straw ashes from a green synthesis
- The obtained amino-silica reduced nitrate content in well water
- The synthesis developed at lab was scalable more than a hundred times.
- The reaction medium was re-used for improving adsorption.
- Sustainability of the synthesis was compared with others.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 July 2021

Received in revised form 8 September 2021

Accepted 9 September 2021

Available online 14 September 2021

Editor: Damia Barcelo

Keywords:

Rice straw

Valorization

Sub-product

Nitrate

Integral water cycle

Adsorption

ABSTRACT

This paper shows a particular example to move to a sustainable circular economical process from valorization of rice straw ashes by developing a green synthesis for obtaining a useful sub-product. This strategy can palliate negative effects of the agriculture waste practices on the environment and also the obtained silica reduced nitrate content in waters. It is demonstrated that the silica synthesis developed at lab was scalable more than a hundred times with good results. Adsorption studies of nitrate in standards and real well waters at lab scale and scaling-up provided similar results. Adsorption values near to 15 mg/g for nitrate standards and 8.5 mg/g for well water were obtained until achieving the initial nitrate concentration. Experimental breakthrough curves fitted to Thomas model, which gave similar results for adsorption capacities. The adsorption capacity was checked with that obtained by a commercial resin, providing improved results. The method at large scale was compared with industrial traditional methods and green adsorbents.

© 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

It is known that agro-wastes need to be treated to minimize their negative impacts on the environment (Vaish et al., 2019). A clear example of that situation is the rice straw. Rice is one of the most consumed crops

* Corresponding author.

E-mail address: pilar.campins@uv.es (P. Campíns-Falcó).

worldwide, Kadam et al. (2000) estimated that for each ton of grains obtained, 1.35 tons of rice straw remained in the fields and around 800 to 1000 million tons per year of rice straw were generated. To manage that waste, farmers incorporate straw into the soil, which is decomposed in fields, causing major die-off of fish and other aquatic fauna in deeper areas (Moliner et al., 2016). Another practice is to eliminate total or partially rice straw by open burning, which is a preferred method because it is inexpensive. However, this method has a detrimental impact on the population and the environment by increasing the atmospheric concentration of harmful gases, mainly carbon dioxide and methane, and at trace levels nitrogen and sulphur compounds, carbon oxide and polycyclic aromatic hydrocarbons (Go et al., 2019), between others. Hence, it is important to provide alternatives for reusing these residues in different ways, such as power generation (Logeswaran et al., 2020; Mahlia et al., 2019) and/or raw materials (Kaur et al., 2017).

In this context, agricultural wastes resulted to be ideal as pollutant adsorbents due to their low cost, local availability, and added economic value (Sulyman et al., 2017). Kyzas and Kostoglou (2014) introduced a new term to refer to those adsorbents as “green” adsorbents and pointed out the need to focus our attention not only on the adsorption of the proposed material, but also its effectivity on scale-up synthesis, from the lab to industry (Gibson, 2014).

Moreover, rice straw is a natural source of silica (Hunt et al., 1983), which is known for being an excellent adsorbent due to its photophysical inertness, chemical stability, and facile surface modification. Despite of this, well-established silica synthesis approaches, including industrial routes, often uses tetraethyl orthosilicate (TEOS) as a precursor (Šoltys et al., 2018; Tanev and Pinnavaia, 1996), which is toxic and expensive. In some cases, these processes are carried out in harmful solvents such as toluene or require the presence of toxic amphiphilic surfactants such as hexadecyltrimethylammonium bromide, CTAB (Ebrahimi-Gatkash et al., 2017). These reagents are also widely used for the synthesis of zeolites and mesoporous materials (Ebrahimi-Gatkash et al., 2017). Nevertheless, the precipitation method (also called neutralization method) from sodium silicate to obtain silica gel is still being the largest share of the global silica market (Flörke et al., 2007; Hyde et al., 2016). It is expected that this method will grow in the next decade, prioritizing those procedures that incorporated more environmental-friendly characteristics to the traditional method (Imyim and Prapalimrunsi, 2010; Ahmaruzzaman and Gupta, 2011; Patwardhan, 2011; Lehman and Larsen, 2014; Hyde et al., 2016).

On the other hand, in a suitable circular economy applied to agriculture (Donner et al., 2020), not only the waste needs to be considered, but also the pollution that farming can cause to the environment. Especially, the use of fertilizers has experienced substantial growth causing harmful effects in the environment, such as water resource pollution. European Directive 98/83/EC on the quality of water intended for human consumption stipulates that nitrate concentration in water must not be higher than 50 mg per liter. High levels of nitrate in water can be dangerous to human health as well as to freshwater- and marine ecosystems. Nitrate can be converted to nitrite, which has the potential to change the hemoglobin in red blood cells into methemoglobin (Klein et al., 2013; Wollin and Dieter, 2005). This process can lead to red blood cells losing the ability to transport oxygen. Moreover, nitrosamines are formed from nitrite by a nitration reaction that can potentially cause cancer of the digestive system. On the other hand, pregnant women may suffer from abortion, intrauterine growth retardation, and central nervous system defects if exposed to a high nitrate environment for a long period (Gao et al., 2020). Several available technologies are used for water treatment of nitrate such as reverse osmosis or biological denitrification, but these methods are expensive, and also generate additional by-products. Contrary, adsorption systems showed to be economical and eco-friendly technologies and it is being extensively used for removing several pollutants of waters.

The objective of this work is to contribute to move towards a sustainable circular economical process in a particular field, starting from valorization of agro-waste and palliating negative effects of the

agriculture on the environment. We used rice straw as a source of silica to develop an adsorbent (Primaz et al., 2021 patent), which reduces the nitrate concentration in waters. The aim of this paper is to analyze the feasibility of valorization rice straw based on sustainability of the silica functionalization process at lab scale and scaling-up. The ability to scale-up the synthesis has been studied according to the principles of green chemistry (Anastas and Warner, 1998) using renewable sources, minimizing reagents, number of steps, and energy consumption, and preventing waste by recycling. Adsorption studies were also carried out and compared with those corresponding to a commercial resin. The EU-funded project LIFE LIBERNITRATE (<http://www.lifelibernitrate.com/>) is using this active silica at a treatment plant for consumption water as a pilot assay for avoiding in place 30% of the current nitrate concentrations from integral water cycle. Both, well water and wastewater of an osmosis plant are being studied.

2. Materials and methods

2.1. Materials and instruments

Rice straw ash (provided by LIFE-Libernitrate project), Potassium nitrate (Merck, Darmstadt Germany), Sodium hydroxide (Sigma-Aldrich, Germany), Hydrochloric acid 37% (Scharlau, Barcelona, Spain), Ethanol (VWR, Chester, USA), Ammonia 25% (Scharlau), 3-aminopropyltriethoxylane (APTES, Merck), Sodium bicarbonate (Scharlau), Sodium chloride (Sigma-Aldrich) and Potassium sulphate (Sigma-Aldrich) were used. Standards of nitrate between 1 and 120 µg/mL were prepared. The water samples were obtained from well water in the municipality of Alginet. These water samples fulfilled European Directive 98/83/EC, an exception was the nitrate concentration which was higher than 50 µg/mL several times during the experimental period. Macroporous resin of polystyrene crosslinked with divinylbenzene functionalized with quaternary ammonium groups (Purolite A520E) from PuroLite (Barcelona, Spain) was used for comparison purposes.

The spectrophotometric measurements between 200 and 400 nm were performed using a CARY UV Visible spectrophotometer model G6860AAR (Agilent Technologies, Santa Clara, USA). A quartz cuvette of 1 cm path length was employed. A wavelength of 220 nm was used for obtaining the calibration graph. MAYA 2000Pro Ocean Optics portable UV-Visible fiber optic spectrophotometer (Ocean Insight, Orlando, USA), which is connected to a DT-MINI-2-GS light source and this in turn to a model T300 optical fiber -RT-UV-Vis was also employed.

FTIR spectra of the silica and amino-modified silica were obtained in the range of 3300–400 cm⁻¹ at a resolution of 4 cm⁻¹ on a Cary 630 FTIR-ATR spectrophotometer Agilent Technologies. For data collection and processing, MicroLab FTIR and Resolution Pro software's (Agilent Technologies) were used, respectively.

Microscopic images of solids were taken with a Nikon microscope ECLIPSE E200LED MV Series (Nikon Corporation, Tokyo, Japan) under bright-field illumination using 10× and 50× objectives.

The specific surface of solids was assessed utilizing the Brunauer–Emmett–Teller (BET) technique, and the pore size distribution was estimated from desorption branches of nitrogen isotherms using the Porosimeter Micromeritics ASAP 2010 02 (Micromeritics, Atlanta, USA).

Morphology of silica and modified silica was studied with a Hitachi S-4800 scanning electron microscope (SEM, Nipon Hitachi, Krefeld, Germany) equipped with energy-dispersive X-ray analysis (EDX) at an accelerating voltage of 10.0 keV over carbon film metalized with a mixture of gold and palladium during 30 s.

The elimination of nitrates in a fixed-bed column was studied using a liquid chromatography column sigma with a length of 10 cm and 0.7 cm of diameter, which was connected with FIA plastic connections to a peristaltic pump MINIPULS 3 (GILSON, Villiers Le Bel, France).

2.2. Preparation of the adsorbent

Two procedures were tested to obtain amino-modified silica from rice straw ashes obtained by thermal decomposition (Primaz et al., 2021). At lab scale 100 g of ashes were treated with 500 mL of 4 M NaOH under refluxing at 95 °C and stirring for 6 h. The resulted mixture was filtered by gravity to obtain a clear yellow solution of silicate.

2.2.1. Procedure 1

Sulphuric acid 4 M was added to silicate solution until pH 7 to obtain silica gel (SiO₂). The gel was dried obtaining crystals and an amount of silica of 62 ± 8 g (n = 10) or 0.12 ± 0.02 g/mL was obtained. Then, the silica (between 1 and 4 g at lab scale and 100–300 g for scaling-up) was modified with amino groups by being rehydrated into hydroalcoholic medium containing APTES and ammonia as a catalyst to obtain the amino-modified silica gel. Table 1 summarized the parameters for the optimization of the synthesis of modified silica: amounts of water, ammonia, APTES and ethanol, all of them expresses per g of silica and the time required for the synthesis.

2.2.2. Procedure 2

Precipitation and amino-modification of the silica were done simultaneously in one step. The sodium silicate solution (between 8 and 33 mL at lab scale and 830 and 2500 mL for scaling-up by using a reactor of 6000 mL) was dispersed in a solution of water, sulphuric acid and APTES. After that, ethanol was added in a controlled rate to form the amino-modified silica gel. The amino-modified silica gel was filtrated, washed and dried to obtain the solid adsorbent material. In order to establish the amount of silica for the synthesis obtained from silicate, 1 mL of obtained solution is taken, which was acidified with H₂SO₄ until pH = 7 and the obtained silica was centrifuged and dried at room temperature and weighed. See Table 1 for the amounts of reagents assayed.

Successive modification on the amino-modified silica layer by layer was also carried out.

2.3. Adsorption studies

2.3.1. Batch assay

An amount of 0.1 g of modified silica of synthesis A10 (see Table 1) was placed into a 4 mL vial and 3 mL of 0.1 M HCl was added and stirred

Table 1

Parameters for the optimization of the amino-silica synthesis and its adsorption capacity until achieving the nitrate initial concentration for well water.

Assay	Procedure	Scale ^a	Reagents g/g silica ^b				Adsorption mg/g silica		
			Water	Ammonia	APTES	Ethanol	Time, h	Layers ^c	
A1	1	Lab	10	1.25	3.1	50	6.5	1	1.27
A2	1	Lab	10	1.25	0.7	50	6.5	1	0.4
A3	1	Lab	10	0.16	0.4	6.25	6.5	1	0.61
A4	1	Lab	2	0.15	0.5	12.5	6.5	1	0.62
A5	1	Lab	5	0.6	3.0	25	6.5	1	0.56
A6	1	Lab	20	1.25	5.1	100	13	2	1.9
A7	1	Lab	30	2.5	9.2	150	19.5	3	3.05
A8	1	Lab	40	3.75	12.3	200	26	4	3.35
A9	1	Lab	50	5	15.4	250	32.5	5	4.11
A10	2	Lab	75	2.5	3.2	22.5	1.5	1	5.09
A11	2	Lab	75	2.5	3.2	22.5	1.5	1	3.67
A12	2	Lab	75	2.5	3.2	22.5	1.5	1	4.64
A13	2	Lab	75	2.5	3.2	22.5	1.5	1	4.8
A14	2	Lab	75	2.5	1.2	22.5	1.5	1	4.9
A15	2	Lab	75	0	3.2	22.5	1.5	1	5.6
A16	2	Lab	75	0	1.6	22.5	1.5	1	2.5
A17	2	Lab	0	0	0	0	1.5	1	0.9
A18	2	Lab	150	5	6.5	45	3	2	8.5
A19	2	Lab	150	5	6.5	45	3	2	10.5
A20	2	Lab	75	5	3.2	22.5	3	2	8.5
A21	2	Lab	150	0	6.5	45	3	2	6.8
A22	1	Scale-up	9.6	1.25	1	45	3	1	3.8
A23	1	Scale-up	0	0	0	0	12	1	0.97
A24	1	Scale-up	9.6	1.25	1	45	8	1	2
A25	1	Scale-up	9.6	1.25	0.5	45	8	1	1.2
A26	1	Scale-up	6.4	0.8	1	30	3	1	3.7
A27	2	Scale-up	30	3	1.5	27	12	1	3.5
A28	2	Scale-up	10	1.2	1	45	6	1	3.11
A29	2	Scale-up	75	2.5	3.2	22.5	2	1	4.6
A30	2	Scale-up	75	2.5	3.2	22.5	2	1	4.9
A31	2	Scale-up	75	2.5	3.2	22.5	2	1	4.8
A32	2	Scale-up	75	2.5	3.2	22.5	2	2	8.5

^a Lab: 1–4 g silica obtained from rice straw in 100–500 mL, large: 100–150 g silica in 6 L, ^b relative concentration of reagents calculated per g of silica, ^c layers; number of successive functionalizations, more than one layers appears in shading, ^d estimated until achieving nitrate initial concentration.

for 3 h to activate the silica. Then, it was centrifuged and washed with water. The activated silica was dispersed in 3 mL of a solution of 25 µg/mL of nitrate and stirred for 10, 30, 60 and 1440 min and after centrifuged at 6000 rpm, 1 mL of the supernatant was collected, and the spectrum was registered between 200 and 400 nm in a quartz cuvette of 1 cm of path length. A nitrate linear calibration up to 50 mg/L at 220 nm was used for nitrate quantifying purposes. The nitrate removal was obtained using Eq. (1).

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where %R = percent of removed nitrate, C_0 = the initial concentration (µg/mL), C_t = concentration of the nitrate anions at t time (µg/mL).

2.3.2. Adsorption isotherms

0.25 g of modified silica (A10, see Table 1) was placed in a liquid chromatography column Sigma with a length of 10 cm and 0.7 cm of diameter and connected with FIA connections to a peristaltic pump (Fig. 1A). The modified silica was activated by recirculating a solution of 1 M HCl at flow rate of 5 mL/min for 1 h. Once the silica was activated, a solution containing nitrate was recirculated for 30 min through the system and after the spectrum was obtained between 200 and 400 nm in order to quantify the adsorbed nitrate concentration. Several concentrations of 0, 25, 50, 75, 100 and 120 µg/mL were tested. Eqs. (2) (Guo and Wang, 2019) and (3) (Singh, 2016) for studying Langmuir and Freundlich models were obtained.

$$q_e = \frac{q_m \times b \times C_e}{1 + b \times C_e} = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e = the equilibrium sorption capacity of sorbent (mg nitrate/g sorbent), C_0 = initial concentration (µg/mL), C_e = the equilibrium concentration of nitrate anion in (µg/mL) after nitrate adsorption, q_m = the maximum amount of anion adsorbed (mg nitrate/g sorbent), b = the factor related with the bonding energy of adsorption in (1/mg), V = treated volume of standard and m = silica mass.

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

where q_e = the equilibrium sorption capacity of sorbent (mg nitrate/g sorbent), C_e = the equilibrium concentration of nitrate anion in (mg/L) after nitrate adsorption, K_f = the adsorption capacity in (mg nitrate/g adsorbent) and n = the adsorption intensity of the sorbent.

2.3.3. Fixed-bed column experiments

Different bed heights of 1.25, 2.3, 3.7 and 7.3 cm, obtained with amounts of modified silica (A13, see Table 1) of 0.25, 0.45, 0.75 and 1.47 g, respectively and various flow rates (5, 5.5, 8, 10, 15 and 22 mL/

min) for a fixed amount of 0.25 g of modified silica were tested for nitrate removal efficiencies by the device shown in Fig. 1B, and by employing a nitrate solution of 26 mg/L.

A quantity of 0.25 g of silica was weighed and activated, and a solution of 50 µg/mL of nitrate was passed until achieving the initial nitrate concentration, using the device of Fig. 1B and the Thomas (de Franco et al., 2018) and Yan (Radnia et al., 2013) models (Eqs. (4) and (5), respectively) were tested. Non-linear fits were obtained from software SOLVER for Microsoft Excel 2021.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left[\frac{K_{Th}}{Q}(q_0 m - C_0 V)\right]} \quad (4)$$

where C_t = the effluent concentration (µg/mL), C_0 = the influent concentration (µg/mL), Q = the flow rate (mL/min), V = the effluent volume (mL), m = the mass of the adsorbent (g), t = time (min), k_{Th} is the Thomas rate constant (mL/min mg), q_0 = the maximum adsorption capacity (mg/g)

$$\frac{C_t}{C_0} = 1 - \frac{1}{1 + \left(\frac{Q C_0 t}{q_y m}\right)^a} \quad (5)$$

where C_0 = the initial solution concentration (µg/mL), Q = the flow rate (mL/min), q_y = the maximum adsorption capacity (mg/g), m = the amount of adsorbent (g), a = Yan model constant.

2.3.4. In-flow nitrate adsorption in standards and well water samples

Several quantities of 0.25 g of silica were weighed and activated, and well samples, nitrate standards and a multicomponent standard (containing 45, 120, 20 and 30 µg/mL of nitrate, bicarbonate, chloride and sulphate, respectively) were processed using the device of Fig. 1B, an UV-vis probe was interfaced in order to monitor the concentration continuously. The same experience was realized by using 0.25 g of commercial resin in the form of chloride. Flow rate of 5 mL/min and a bed height of 2.3 cm were employed for both, silica and resin.

A silica sample of 0.25 g previously saturated with well water was processed with sodium hydroxide 0.1 M for 60 min at a flow rate of 5 mL/min by using the device of Fig. 1A, an aliquot was taken every 5 min and nitrate concentration was measured. Regenerated silica was activated and reused for nitrate adsorption by using the lab manifold of Fig. 1B as mentioned above. These steps were repeated three times.

3. Results and discussion

3.1. Optimization of the amino-silica synthesis and scale up possibilities

The selected method for the synthesis of the silica from rice straw ashes was the neutralization method with H_2SO_4 acid until pH 7 due

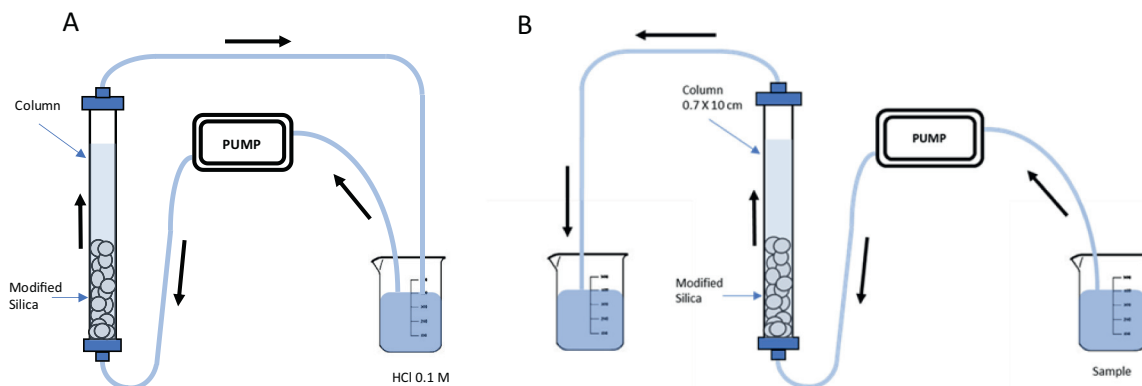


Fig. 1. Lab manifolds for testing nitrate adsorption: A) for silica activation and establishing of adsorption isotherms and B) for in flow nitrate adsorption studies and breakthrough curves.

to it is one of the most used methods for silica synthesis, so improvements applied through greener synthesis could be implemented widely and faster than using other methodologies. Silicic acid concentration greater than the solubility limit of silica leads to its polymerization and precipitation (Hyde et al., 2016). Chemical and structural characteristics of the silica such as porosity and particle size are affected by factors such as reactant concentrations, temperature, time of stirring and addition of reagents for functionalizing or impregnating the silica surface.

Fig. 2 shows the flow charts for the two procedures that were studied in this work to obtain amino-modified silica from rice straw ashes (Primaz et al., 2021 patent).

Firstly, the assays were carried out using small quantities in the lab or small scale and then, it was moving to higher amount as it can be seen in Table 1 named scale-up. The quantities used at small scale were accommodated to the conditions of the process at higher scale and the results obtained, as well as the problems or limitations found, were resolved at lab scale and then, moved to higher scale in order to avoid wastes and reduce economic costs.

The studied parameters for obtaining the modified silica were the amounts of water, ammonia, APTES and ethanol, all of them expressed per g of silica (see Section 2.2, Table 1) and, also, the time required for the synthesis. We selected APTES because is greener than ternary and quaternary ammonium tags. Water well samples were employed in order to provide a more realistic nitrate adsorption values, due to natural waters contained other anions (as sulphate, phosphate, bicarbonate, iodure), which can affect the adsorption capacity of the material as demonstrated in following sections. The assays were carried out on the fixed-bed column in flow mode (see Fig. 1B) at lab-scale. Adsorption values were calculated considering the amount of nitrate retained at each point assayed until achieving the initial concentration of nitrate. The intercept, slope and determination coefficient of the calibration graph used for obtaining the nitrate concentration were: $b_0 \pm s_{b_0} = 0.04 \pm 0.05$; $b_1 \pm s_{b_1}(\text{mL}/\mu\text{g}) = 0.053 \pm 0.01$ and $R^2 = 0.996$, respectively.

The adsorption capacities of the amino-silica for well water obtained by procedure 1 varied from 0.5 to 1.3 mg nitrate/g modified silica as it can be seen in the assays A1-A5 of Table 1, while for procedure 2 provided adsorptions varying from 3.7 to 5.6 mg/g at lab scale (A10-A15). Therefore, procedure 2 produced amino-modified silica with higher

capacity of adsorption at lab scale level (Table 1). Other advantages of the use of procedure 2 are the reduction of time from 6.5 h, required for procedure 1, to 1.5 h. This is because in procedure 1 a previous step for dispersion and rehydration of the SiO_2 (5 h) is needed, and in procedure 2 the precipitation and functionalization were carried out in one step (1.5 h).

Another parameter is the amount of APTES used per g of silica. It was observed that an increment of amount of APTES in the synthesis increased the adsorption capacity of the amino-silica especially for the procedure 1 as Table 1 indicates (A6-A9). Using more than two times the amount of APTES per g of silica produced adsorbents with increased capacity of adsorption.

For procedure 2, it was observed the same trend at lab scale; two layers achieved almost double adsorption capacity as results of A18-A21 indicated (see Table 1). We can also see how using the procedure 1, the capacity adsorption (4.1 mg/g of nitrate for A9) for 5 layers is the same as one layer for the amino-modified silica by procedure 2 (see A10-A15 in Table 1). These results demonstrated that procedure 2 was more effective not only for obtaining the first modification also for its second modification. Procedure 2 achieved the highest adsorption, which was around 10 mg nitrates/g in only two layers for well water samples. Note that the minimum amount of APTES giving good results was 3.3 g/g de silica (see Table 1).

For scaling-up, several syntheses (A22-A32 of Table 1) were carried out considering the results at lab scale and similar conclusions were established. Procedure 2 (A29-A32) gave the best results by employing the same reagent proportions than those optimized at lab scale (A10-A13, A20). These results indicated a good scalability of the conditions established at lab.

Ammonia is used as a catalyst in the sol-gel reaction to incorporate the APTES to the silica, but this reaction can be carried out using acid as a catalyst too. In procedure 2, both steps, precipitation and modification, were made in one step and the medium for silica modification become acid due to the presence of sulphuric acid. Therefore, we tested the possibility to avoid ammonia in the procedure by considering that the sulphuric acid can act as a catalyst. The modified silica obtained by this method showed similar adsorption to that obtained in presence of ammonia, see A15 and A10-13 in Table 1.

Finally, standing on our idea of development of a green method of synthesis, we go a step further and we tested the possibility of reuse

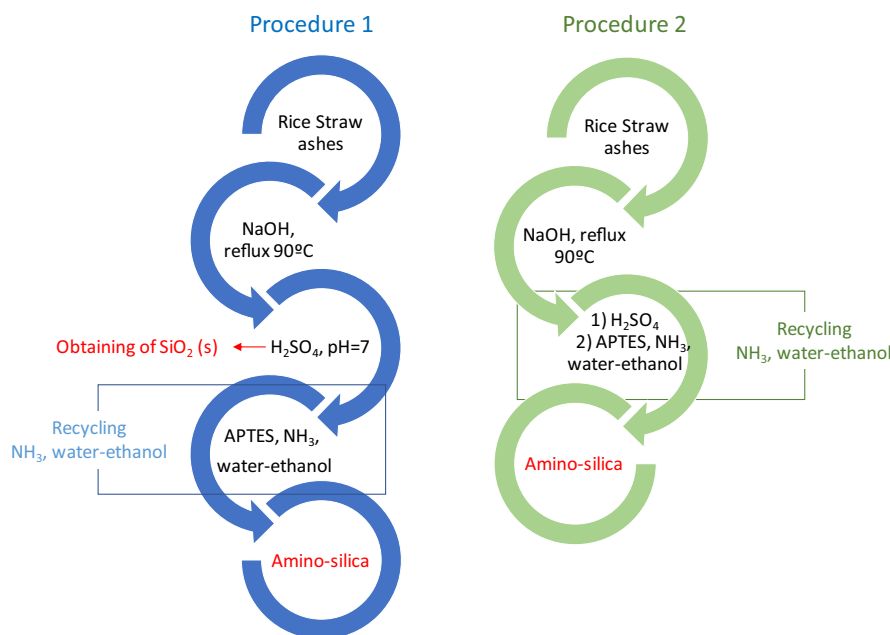


Fig. 2. Flow Chart of the experimental procedures used with (a) and without (b) silica separation before its modification.

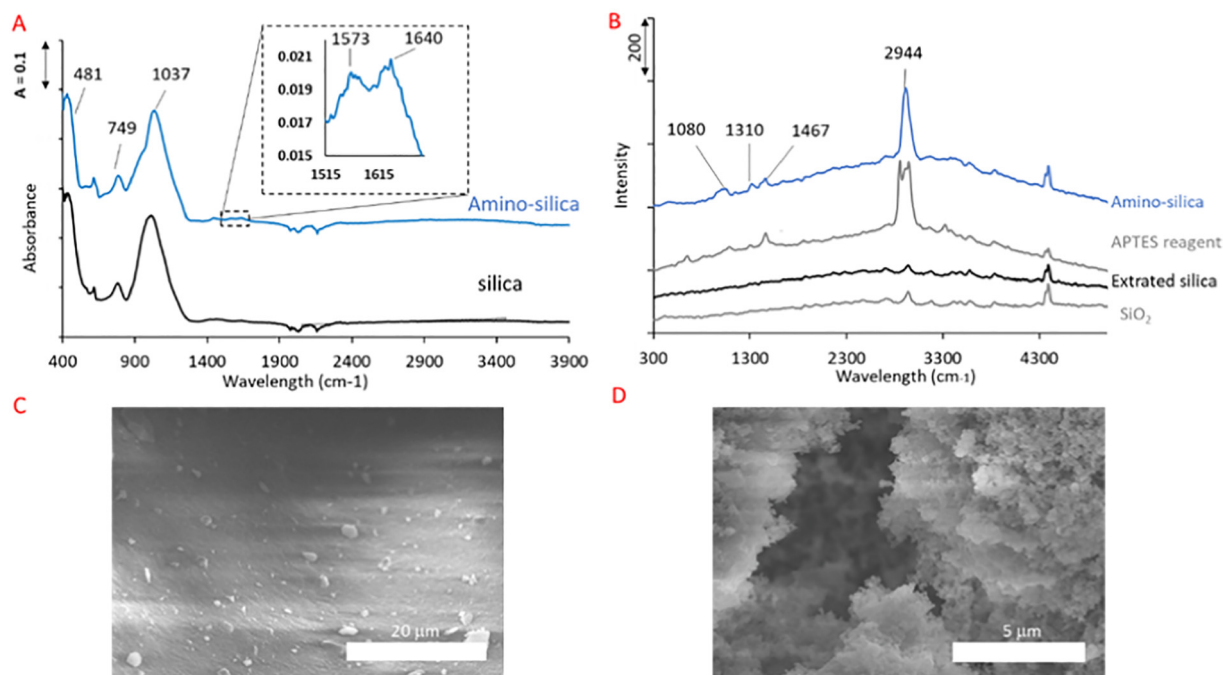


Fig. 3. A) FT-IR spectra of extracted silica and amino-silica, B) Raman spectra of amino-silica, APTES reagent, extracted silica and commercial silica, C) SEM images of the extracted silica and D) SEM images of the obtained amino-silica.

the medium of reaction of silica modification (ethanol, water and remaining APTES) for new synthesis or for the modification of already modified silica. For new synthesis the results were discrete as A17 and A23 synthesis show in Table 1 for lab and large scales. A second layer modification carried out with recycled medium gave similar adsorption than non-recycled or fresh medium, see A20 assay of Table 1, which gave similar values of adsorption than A18-19. Therefore, the recycled medium can be used for increasing the adsorption of modified silica by adding layers without consuming more reagent/solvents and without generation of more wastes.

3.2. Characterization of the modified silica

Fig. 3A shows the infrared spectra obtained for the silica and modified silica. In both spectra it can be seen the vibration bands at 481 and 795 cm^{-1} , which are attributed to the deformation and regular stretching Si—O, respectively and the band at 1037 cm^{-1} was assigned to the major asymmetric stretching of Si-O-Si (Le et al., 2013). Amino-functionalized silica shows two bands in the region 1650–1580 cm^{-1} , that were not observed on silica spectrum, and corresponded to N—H bending vibration of primary amine. These bands are indicative of a successfully incorporation of amino groups on the silica by its functionalization with APTES (Le et al., 2013).

Fig. 3B shows Raman spectra of extracted silica, amino-silica, APTES and a commercial silica (SiO_2 mesh X). The incorporation of APTES on silica surface to obtain amino-silica can be confirmed by the presence of characteristic bands such as very strong band at 2944 cm^{-1} assigned to the asymmetric stretching of CH_2 , a strong band at 1467 cm^{-1} indicating the Si- CH_2 bond (Sun et al., 2017), a band at 1310 cm^{-1} attributed to NH_2 (Jaramillo et al., 2017), and a band at 1080 cm^{-1} assigned to Si-O-C (De Oliveira et al., 2008).

The morphologies of the silica and the modified silica were analyzed by scanning electron microscopy (SEM). The images are presented in Fig. 3 C and D, which show that a porous material was obtained after amino modification of the silica while the silica showed a smooth surface. Also, the specific surface and pore size distribution and the total volume of the porous of several obtained amino-silica samples were

analyzed by BET. The surface areas for the different silica were in the range of 194 to 75 m^2/g (Table 2), which is in accordance to the method of preparation used by precipitation (Patwardhan, 2011). Amino-silica analyzed showed a porous size lower than 20 nm, compatible with a mesoporous material (Beck et al., 1992; Cashin et al., 2018; Zhao et al., 1998).

The activation of modified silica was carried out with HCl 1 M (see Section 2.3). After activation, amino-silica was analyzed by SEM/EDX (Fig. 4) and elemental analysis. Activated amino-silica retained chloride (Fig. 4A) on its surface. The activated adsorbent was used for removal nitrate from the well water and after adsorption was analyzed by SEM/EDX and elemental analysis too. Fig. 4B shows an increase of the percentage of oxygen and a decrease of the percentage of chloride (from 4.43 to 0.00%) with respect to Fig. 4A, which is indicative of the adsorption of nitrate on the adsorbent surface. These results suggested that the adsorption of the nitrate can be produced by ionic exchange as expected, nitrate anions displaced chlorine anions during the adsorption process (see Fig. 5).

3.3. Characterization of the adsorption profile of the modified silica

The effect of time on adsorption of the active modified silica was studied in a batch system (see Section 2.3). The removal efficiency increased up to 10 min reaching 85–90%. Then, the removal efficiency

Table 2
Physical properties and adsorption of modified and unmodified silica.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Pore size BET (nm)
Amino-silica ^a	194	0.470	15.85
Amino-silica ^b	144	0.312	8.65
Amino-silica ^b	92	0.210	14.02
Amino-silica ^c	75	0.121	6.55

^a One layer amino-silica at lab scale.

^b Two layer amino-silica at lab scale.

^c One layer amino-functionalized obtained at higher scale.

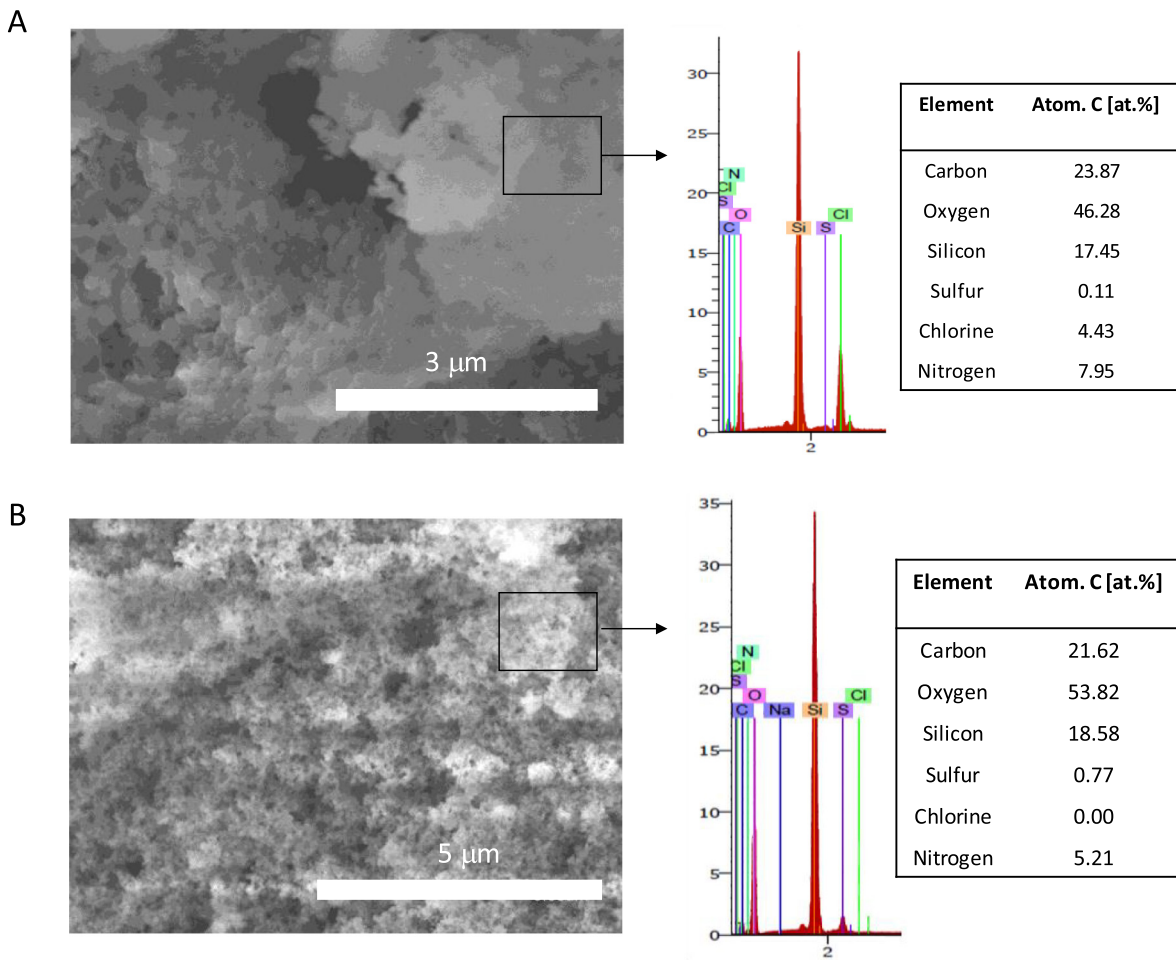


Fig. 4. SEM images/EDX micrograph of activated amino-silica A) before and B) after adsorption of nitrates.

remained stable until 30 min and after 120 min, decreased to values below 30%.

To investigate the behaviour of nitrate adsorption in flow mode, adsorption was studied using the proposed device shown in Fig. 1B. A given amount of silica was placed into a column and continuous flow of a nitrate solution pumped with a peristaltic pump. The optimal conditions of the system according to the bed height and flow

rate were studied. The effect of the amino-silica bed height on nitrate adsorption in fixed-bed column was investigated using different heights (see Section 2.3) at a constant flow rate of 5 mL/min for a standard solution containing 26 μg/mL of nitrate. The removal efficiency is shown in Fig. 6A. From this figure, it can be observed that efficiency removal increased by increasing the bed height from 1.25 to 2.3 cm and then, remained constant. Therefore, the optimal

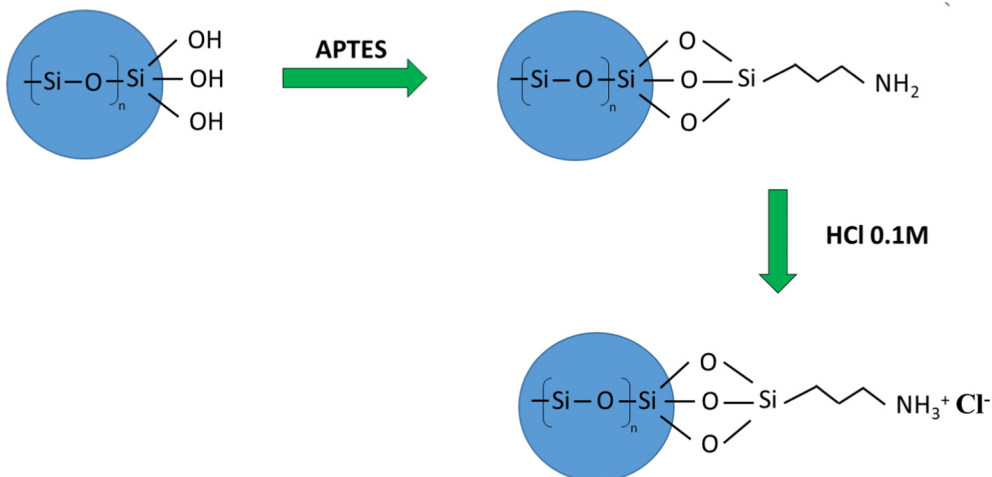


Fig. 5. Activated form of the modified silica as an anionic exchanger.

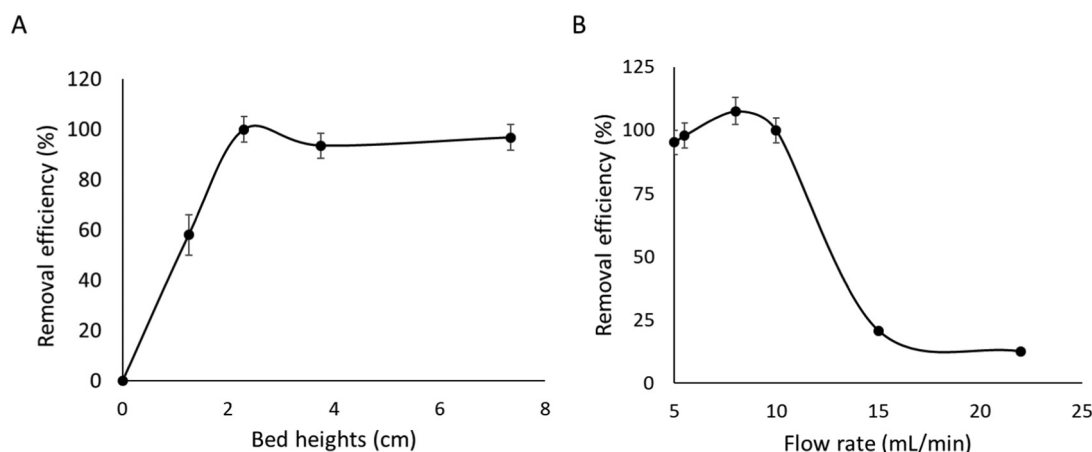
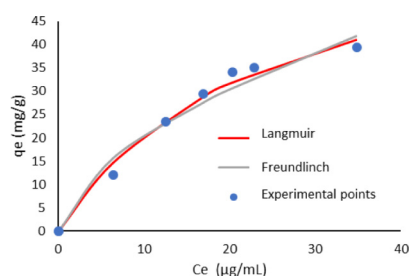


Fig. 6. A) Effect of bed heights (cm) and B) effect of flow rate on removal efficiency of nitrate by the amino-silica in fixed-bed column system. (n = 3). For more explanations see text.



Langmuir model			Freundlich model		
qm, mg/g	b, l/mg	R ²	K _f	n	R ²
68.5	0.043	0.99	5.38	1.7	0.97

Fig. 7. Experimental and theoretical adsorption isotherm of nitrate anion on modified silica at several concentrations assayed between 0 and 120 µg/mL, and Langmuir and Freundlich models for nitrate anion removal. See Section 2.3 for more explanation.

taking up of adsorbent into the column result is about one fifth of the total column.

The effect of flow rate was examined between 5 and 25 mL/min at a constant nitrate concentration of 26 µg/mL and 2.3 cm of bed height (Fig. 6B). The results indicated that the removal efficiency of nitrate was not significantly influenced by the flow range assayed up to 10 mL/min. Nitrate adsorption by amino silica is affected by insufficient contact time between the adsorbent and the nitrate in the column at the higher flows assayed as it can be seen in Fig. 6B.

Fig. 7 shows the experimental and theoretical values for the adsorption of nitrate with a quantity of 0.25 g of modified silica A12 (see Table 1 and Fig. 1B) at a temperature of 25 °C (see Section 2.3) for several standards of nitrate between 0 and 120 µg/mL. The b, q_m, n, K_f values and the coefficient of determination (R²) for Langmuir and Freundlich isotherms are given in Table 3. The coefficient of determination

Table 3
Parameters for the optimization of the amino-silica synthesis and its adsorption capacity.

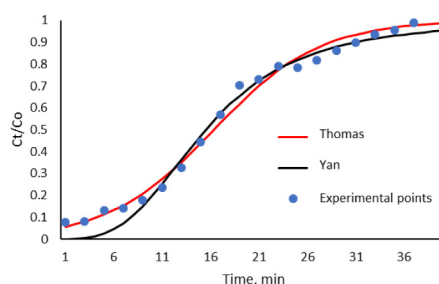
Adsorbent	Langmuir q _m (mg/g)	Initial concentration (µg/mL)	Contact time (min)	T °C	Ref.
DMDAC-Silica gel	39.3	100	180	30	Kang et al., 2019
NN-MCM-41	38.6	30–250	120	25	Ebrahimi-Gatkash et al., 2017
SBA-15	136	10–1000	180	30	Kang and Kim, 2020
RSi-bPEI	116	50	90	–	Suzaimi et al., 2019
Amino-silica	68.5	25–120	30	25	This study

indicated that the adsorption was fitted better by the Langmuir model (R² = 0.99) than by the Freundlich model (R² = 0.97). This behaviour suggested that a monolayer adsorption of nitrate onto the surface of amino-silica was achieved (Langmuir, 1918; Munagapati and Kim, 2017). The maximum adsorption capacity (q_m) by Langmuir model was determined as 68.5 mg of nitrate/g of modified silica.

In general, the adsorption capacity expressed as q_m obtained was in the range of other adsorbents reported as Table 3 shows. The material obtained in this work shows some advantages over the new materials proposed recently shown in Table 3. It shows a high adsorption capacity expressed as Langmuir q_m in a shorter time, besides its synthesis used as raw material (extracted silica) a by-product generated from the rice straw. On the other hand, the modification process is carried out under standard conditions of pH and temperature. In addition, APTEs as a modifier is more environmentally friendly product than tertiary and quaternary amines.

The dynamic adsorption process is important in the characterization of porous materials (see Table 2), it is studied by breakthrough curves, which indicates the adsorption concentration in the effluent at the outlet of a fixed-bed adsorbent (Aksu and Gonen, 2004).

A bed height of 2.3 cm was used in a column at 25 °C (see Fig. 1B), a standard solution of 40 µg/mL of nitrate was passed through at a flow rate of 5 mL/min (0.25 g of synthesis A12 of Table 1 was used). Breakthrough curve was fitted well to sigmoidal-type mathematical models, namely, Thomas and Yan models (Eqs. (4) and (5), respectively) and



Thomas model			Yan model		
kth (mL/h/g)	qth (mg/g)	R ²	a	qy (mg/g)	R ²
4.75	12.5	0.99	3.18	11.8	0.93

Fig. 8. Experimental breakthrough curve for modified silica and Thomas and Yan models for nitrate anion removal.

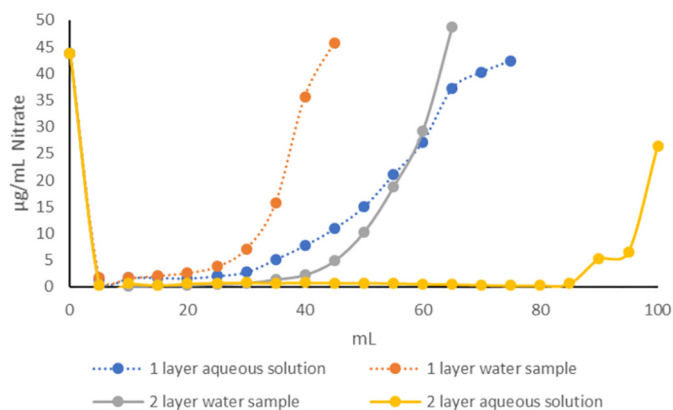


Fig. 9. Adsorption of nitrates in aqueous solution of 45 µg/mL and samples of water for one- and two-layer silica. Nitrate concentration vs mL of processed water.

the adsorption capacity was calculated based on the fitting results, see Fig. 8.

According to the coefficient of determinations of Thomas ($R^2 = 0.99$) and Yan ($R^2 = 0.93$) models, the adsorption behaviour is more in line with the Thomas model, which accepts Langmuir adsorption and desorption kinetics and no axial dispersion (Chu, 2010). The quantity of nitrate uptake predicted by this model was 12,5 mg/g for the standard solution assayed (see Fig. 8).

3.4. In-flow nitrate adsorption in standards and well water samples

A well water sample containing nitrate in a concentration of 45 µg/mL was analyzed by using the proposed device shown in Fig. 1B at lab scale, and the results were compared with the adsorption capacity values obtained using a nitrate standard solution of 45 µg/mL. For these experiments one layer (A14 in Table 1) and two layer (A18 in Table 1)

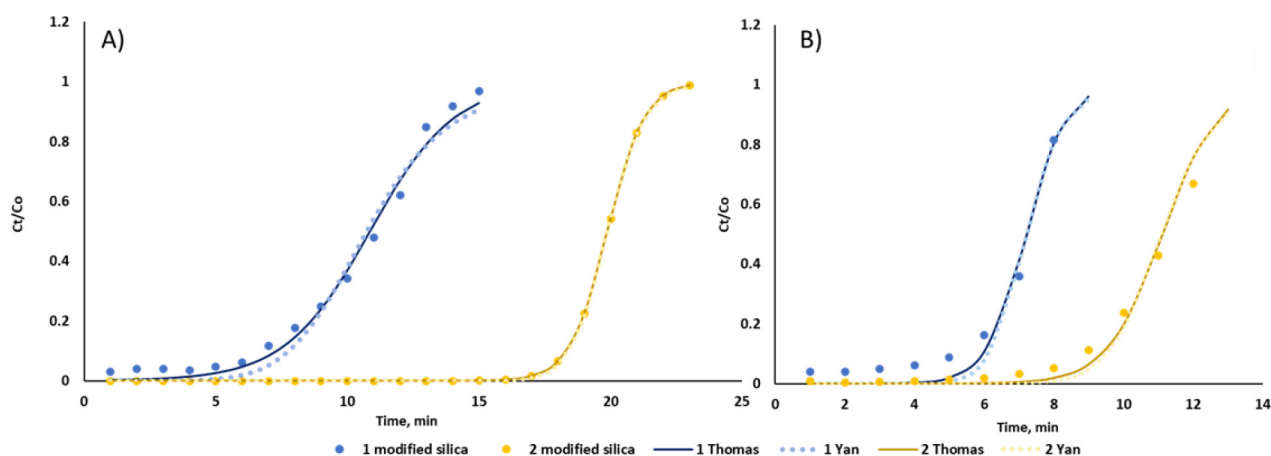
modified amino-silica were employed. The results showed in Fig. 9 provided adsorption capacity values calculated as the amount of nitrate retained until achieving the concentration of the standard solution for one-layer silica and two-layer of silica, being 8.3 and 15.2 mg/g, respectively. It can be seen that amino-silica that has been modified two times achieved almost double adsorption capacity than the amino-silica modified once.

According to the adsorption capacity values of amino-silica in well water sample, it can be seen that the adsorption capacity decreased obtaining 4.9 and 8.5 mg/g for one-layer silica and two-layer of silica, respectively (see Table 1). This decrease can be produced due to the presence of other anions in water samples, which can negatively influence the adsorption processes of nitrates. A multicomponent standard containing 45 µg/mL of nitrate and other anions at concentration levels similar to those present in the well sample (see Experimental section 2.3.4) was tested using the two-layer silica. The adsorption capacity obtained for nitrate was 10 mg/g, this value supported the lower absorption values obtained in the well water in reference to nitrate standards and the mechanisms of the adsorption (see Fig. 5).

Fig. 10 shows the Thomas and Yan models which are in accordance with those shown in Fig. 8 for A12 synthesis of Table 1 by working with a standard solutions. Similar results were obtained by using these models than estimating the nitrate adsorption by point by point from the results given in Fig. 9.

The mean value for nitrate adsorption provided by A10- A15 synthesis of Table 1 was 4.7 ± 0.6 mg/g silica for well water, providing a good precision. Similar values of precision were obtained for large scale, nitrate adsorption provided by synthesis A28-A31 shown in Table 1 were 4.8 ± 0.3 mg/g silica.

The regeneration performance of the modified silica with sodium hydroxide (see Section 2.3) was assayed with well water. The treatment was effective processing the sample for 10 min. Three cycles were assayed and the absorption values were $90 \pm 10\%$ of that achieved in



Sample	Layers	Thomas model			R^2	Yan model		
		kth (mL/h/g)	qth (mg/g)	a		qy (mg/g)	R^2	
Standard	1	14.44	9.34	0.99	6.82	9.41	0.98	
	2	32.77	17.10	0.99	28.24	17.40	0.99	
Water	1	40.97	6.20	0.98	13.55	6.30	0.97	
	2	29.40	9.56	0.96	14.31	9.70	0.95	

Fig. 10. Experimental breakthrough curve for modified silica analysis of Thomas and Yan models. 1 (one layer), 2 (two layer) A) standard of 45 µg/mL and B) sample of water.

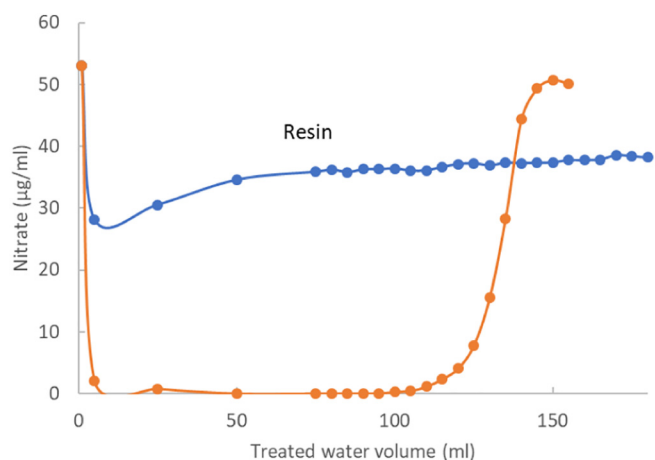


Fig. 11. Continuous monitoring of nitrate concentration for a well water sample by using activated silica and a commercial resin. For working conditions see Experimental section.

a single use. This experiment shows that the modified silica can be re-used at least three times.

The same amount of active silica and a commercial resin (0.25 g) was used for studying adsorption of nitrate in a well water sample containing 53 µg/mL of nitrate. Active silica removes a higher percentage of nitrates from the water as it is shown in Fig. 11. In the interval 0.5 to 22 min, the nitrate concentration is 1 µg/mL if modified silica was used as adsorbent, meanwhile for the resin nitrate concentration was

near 38 µg/mL. The adsorption kinetics is faster for silica than for resin as can be seen in Fig. 11.

3.5. Sustainability of the process in comparison with other methods for silica preparation

The principles of green chemistry were introduced in the early 1990's and articulate the objective of reducing (and/or eliminating) negative environmental impacts by decreasing waste or increasing efficiency of chemical processes or syntheses (Anastas and Warner, 1998).

The topics of greener syntheses, environmental applications and biological toxicity were reviewed by Lehman and Larsen, 2014 in the case of zeolite and mesoporous silica nanomaterials. Our method at large scale was compared with industrial traditional methods and recently published works about green adsorbents. Some characteristics of those methods are summarized in Table 4. One sustainable characteristic of our method was the use of silicate from agro-waste making the process greener. Another difference is that in the same step of silica precipitation, APTES and ethanol were added to obtain amino-functionalized silica adsorbent.

Compared with the green methods reported, we can see that the use of agricultural residue as a source of silica is not new (Balajirao, 2012), especially for rice husk which was used as a source of silica (Ahmaruzzaman and Gupta, 2011), in contrast our method proposes the use of straw rice which can solve the problem of the air contamination by its burning. Respect to the green characteristics of proposed method compared to the others; the time is 8 h while in most of them required 24 h, only one method is proposed employing 3 h but, in

Table 4

Comparison of traditional methods in industry (in blue), new green lab-scale methods (in white) with our green large-scale methods for synthesis of modified silica. Some of these materials were used as adsorbents.

Silica source/REF	Reagent	Solvent	Reaction conditions Synthesis			By-product	Silica type	Application
			T, h	T, °C	pH			
TEOS (Zhao et al., 1998)	Pluronic	Water	44 +6	44–100, 500	<7	Alcohol, NO _x , CO ₂ , Na ₂ SO ₄	Mesoporous SBA-15	–
TEOS (Tanev and Pinnavaia, 1996)	Dodecyl -amine	Water, ethanol	18 +6	20, 500	9	No reported	Mesoporous HMS	–
TEOS (Šoltys et al., 2018)	CTAB, NH ₃	Water, ethanol	3+ 6+ 6	20, 200, 600	7–10	No reported	Mesoporous silica MS	–
Silicate (Beck et al., 1992)	CTAB, ammonia	Water	0.5 +1 68	20, 500	9	Ethanol, NO _x , CO ₂ ,	Mesoporous MCM-41	–
Silicate (Flörke et al., 2007)	H ₂ SO ₄	Water	3+ 5	35–80	7	Na ₂ SO ₄	Precipitated industrial gel	–
TEOS (Ebrahimi-Gatkash et al., 2017)	CTAB, APTES	Toluene	>9 6+ 6	110, 540		No reported	Mesoporous MCM-41	Removal nitrates
Agro-waste ash (Vaibhav et al., 2015)	NaOH, H ₂ SO ₄	Water	24 +1 2	Drying, rt aging	7	Na ₂ SO ₄	Silica xerogel	–
Rice Husk ash (Imyim and Prapalimrunsi, 2010)	APTES	Toluene, in N ₂	24	90–100		Ethanol	Amorphous silica	Removal humic acid
Ash rice and clay (Balajirao, 2012)	APTES	Water	3	25–200		Ethanol	Powder (size: 10– 800 nm)	Water disinfection
Rice straw ash (this work)	NaOH, H ₂ SO ₄ , APTES	Water, ethanol recycled	6+ 2	90, rt	>7	Na ₂ SO ₄ , Ethanol	Amino- silica mesoporous	Remove nitrate in waters

contrast, it required higher temperatures (200 °C). In addition, our method allows recycling the medium of reaction to carry out several layers of modified silica.

4. Conclusions

A sub-product from rice straw ashes was obtained and proved useful for adsorption of nitrate from water. The use of straw rice can solve the problem of the air contamination by its burning in the field. Two methods were studied for amino-silica synthesis and the procedure employing silicate permitted to carry out the modification with APTES in only one step and saving time, 1.5 h vs 6.5 h (including a step for silica crystallization previously to modify it) and at room temperature. We selected APTES because is more sustainable than ternary and quaternary ammonium tags. It is possible to re-use the reaction medium in order to improve the adsorption capacity by generating several layers.

Amino-silica showed a porous size lower than 20 nm, compatible with a mesoporous material. It shows a high adsorption capacity expressed as Langmuir q_m in a short time. We demonstrated that the synthesis at lab is scalable by a factor around 100 employing only 2 h. Adsorption studies of nitrate in standards and real well waters at lab scale and scaling-up provided similar results. Adsorption values near to 15 mg/g for nitrate standards and 8.5 mg/g for well water were obtained until achieving the initial nitrate concentration. Experimental breakthrough curves fitted to Thomas model gave similar results for adsorption capacities. The adsorption capacity of silica was higher than that achieved by a commercial resin used for potable water treatment.

The scaled-up method was compared with industrial traditional methods and recently published works about green adsorbents. One sustainable characteristic of our method was the use of silicate from agro-waste making the process greener. Another difference is that in the same step of silica precipitation, APTES and ethanol were added to obtain amino-functionalized silica adsorbent. The time is 8 h (6 h for obtaining the silica from rice straw ashes and 2 h for amino-silica product) while in most of the reported methods required 24 h, only one method is proposed employing 3 h but, in contrast, it required higher temperatures (200 °C) and it is for water disinfection. In addition, our method allows recycling the medium of reaction.

CRedit authorship contribution statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript.

Declaration of competing interest

The authors declare that there is no conflict of interest.

Acknowledgements

The authors are grateful to EU (EASME LIFE and CIP ECO-Innovation) LIBERNITRATE. LIFE 16 ENV/ES/000419; EU FEDER and the Gobierno de España MCIU-AEI (CTQ2017-90082-P) and the Generalitat Valenciana (PROMETEO 2020/078) and EU FEDER- Generalitat Valenciana (ID-FEDER/2018/049) for the financial support received. H. R. Robles-Jimarez expresses his grateful to EU-LIBERNITRATE. L. Sanjuan-Navarro expresses his gratitude for the FPU-grant (MCIU-AEI).

References

Ahmaruzzaman, M., Gupta, V.K., 2011. Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. *Ind. Eng. Chem. Res.* 50, 13589–13613.
 Aksu, Z., Gönen, F., 2004. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochem.* 39, 599–613.

Anastas, P.T., Warner, J.C., 1998. *Green Chemistry: Theory and Practice*. Oxford University Press.
 Balajirao, S., 2012. Method for purifying water by contacting water with a porous rice husk ash and clay mixture and apparatus therefore Patent Publication Number: WO/2012/025943.
 Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., Schlenker, J.L., 1992. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* 114, 10834–10843.
 Cashin, V.B., Eldridge, D.S., Yu, A., Zhao, D., 2018. Surface functionalization and manipulation of mesoporous silica adsorbents for improved removal of pollutants: a review. *Environ. Sci. Water Res. Technol.* 4, 110–128.
 Chu, K.H., 2010. Fixed bed sorption: setting the record straight on the Bohart-Adams and Thomas models. *J. Hazard. Mater.* 177, 1006–1012.
 De Franco, M.A.E., De Carvalho, C.B., Bonetto, M.M., De Pelegrini Soares, R., Férís, L.A., 2018. Diclufenol removal from water by adsorption using activated carbon in batch mode and fixed-bed column: isotherms, thermodynamic study and breakthrough curves modeling. *J. Clean. Prod.* 181, 145–154.
 De Oliveira, A.A.R., Ciminelli, V., Dantas, M.S.S., Mansur, H.S., Pereira, M.M., 2008. Acid character control of bioactive glass/polyvinyl alcohol hybrid foams produced by sol-gel. *J. Sol-Gel Sci. Technol.* 47, 335–346.
 Donner, M., Gohier, R., de Vries, H., 2020. A new circular business model typology for creating value from agro-waste. *Sci. Total Environ.* 716, 137065.
 Ebrahimi-Gatkash, M., Younesi, H., Shahbazi, A., Heidari, A., 2017. Amino-functionalized mesoporous MCM-41 silica as an efficient adsorbent for water treatment: batch and fixed-bed column adsorption of the nitrate anion. *Appl. Water Sci.* 7, 1887–1901.
 Flörke, O.W., Graetsch, H.A., Brunk, F., Benda, L., Paschen, S., Bergna, H.E., Roberts, W.O., Welsh, W.A., Chapman, D.M., Ettlinger, M., Kerner, D., Maier, M., Meon, W., Schmoll, R., Gies, H., Schiffmann, D., 2007. *Silica*. Ullmann's Encycl. Ind. Chem. Wiley-VCH Verlag.
 Gao, S., Li, C., Jia, C., Zhang, H., Guan, Q., Wu, X., Wang, J., Lv, M., 2020. Health risk assessment of groundwater nitrate contamination: a case study of a typical karst hydrogeological unit in East China. *Environ. Sci. Pollut. Res. Int.* 27, 9274–9287.
 Gibson, L.T., 2014. Mesosilica materials and organic pollutant adsorption: part B removal from aqueous solution. *Chem. Soc. Rev.* 43, 5173–5182.
 Go, A.W., Conag, A.T., Igdon, R.M.B., Toledo, A.S., Malila, J.S., 2019. Potentials of agricultural and agro-industrial crop residues for the displacement of fossil fuels: a Philippine context. *Energy Strat. Rev.* 23, 100–113.
 Guo, X., Wang, J., 2019. Comparison of linearization methods for modeling the Langmuir adsorption isotherm. *J. Mol. Liq.* 296, 111850.
 Hunt, L.P., Amick, J.A., Dismukes, J.P., 1983. Rice hulls as a raw material for producing silicon. *Conference on Materials and New Processing Technologies for Photovoltaics*, San Francisco, CA, USA.
 Hyde, E.D.E.R., Seyfaee, A., Neville, F., Moreno-Atanasio, R., 2016. Colloidal silica particle synthesis and future industrial manufacturing pathways: a review. *Ind. Eng. Chem. Res.* 55, 8891–8913.
 Imyim, A., Prapalimrungsi, E., 2010. Humic acids removal from water by aminopropyl functionalized rice husk ash. *J. Hazard. Mater.* 184, 775–781.
 Jaramillo, A.F., Baez-Cruza, R., Montoya, L.F., Medinam, C., Pérez-Tijerina, E., Salazar, F., Rojas, D., Melendrez, M.F., 2017. Estimation of the surface interaction mechanism of ZnO nanoparticles modified with organosilane groups by Raman Spectroscopy. *Ceram. Int.* 43, 11838–11847.
 Kadam, K.L., Forrest, L.H., Jacobson, W.A., 2000. Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects. *Biomass Bioenergy* 18, 369–389.
 Kang, J.K., Kim, S.B., 2020. Synthesis of quaternized mesoporous silica SBA-15 with different alkyl chain lengths for selective nitrate removal from aqueous solutions. *Microporous Mesoporous Mater.* 295, 109967.
 Kang, J.K., Lee, S.C., Kim, S.B., 2019. Synthesis of quaternary ammonium-functionalized silica gel through grafting of dimethyl dodecyl [3-(trimethoxysilyl)propyl]ammonium chloride for nitrate removal in batch and column studies. *J. Taiwan Inst. Chem. Eng.* 102, 153–162.
 Kaur, D., Bhardwaj, N.K., Lohchab, R.K., 2017. Prospects of rice straw as a raw material for paper making. *Waste Manag.* 60, 127–139.
 Klein, B.E.K., McElroy, J.A., Klein, R., Howard, K.P., Lee, K.E., 2013. Nitrate-nitrogen levels in rural drinking water: is there an association with age-related macular degeneration? *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 48, 1757–1763.
 Kyzas, G.Z., Kostoglou, M., 2014. Green adsorbents for wastewaters: a critical review. *Mater. (Basel, Switzerland)* 7, 333–364.
 Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40, 1361–1403.
 Le, V.H., Thuc, C.N.H., Thuc, H.H., 2013. Synthesis of silica nanoparticles from vietnamese rice husk by sol-gel method. *Nanoscale Res. Lett.* 8, 58.
 Lehman, S.E., Larsen, S.C., 2014. Zeolite and mesoporous silica nanomaterials: greener syntheses, environmental applications and biological toxicity. *Environ. Sci. Nano* 1, 200–213.
 Logeswaran, J., Shamsuddin, A.H., Silitonga, A.S., Mahlia, T.M.L., 2020. Prospect of using rice straw for power generation: a review. *Environ. Sci. Pollut. Res.* 27, 25956–25969.
 Mahlia, T.M.L., Logeswaran, Anwar, M., Rahman, M.M., Shamsuddin, 2019. Potential of rice industry biomass as a renewable energy source. *Energies* 12, 4116.
 Moliner, C., Bosio, B., Arato, E., Ribes, A., 2016. Thermal and thermo-oxidative characterization of rice straw for its use in energy valorisation processes. *Fuel* 180, 71–79.
 Munagapati, V.S., Kim, D.S., 2017. Equilibrium isotherms, kinetics, and thermodynamics studies for Congo red adsorption using calcium alginate beads impregnated with nano-goethite. *Ecotoxicol. Environ. Saf.* 141, 226–234.

- Patwardhan, S.V., 2011. Biomimetic and bioinspired silica: recent developments and applications. *Chem. Commun.* 47, 7567–7582.
- Primaz, C.T., Jornet-Martínez, N., Sanjuan-Navarro, L., Moliner-Estopiñán, C., Campins-Falcó, P., Molins-Legua, C., Ribes-Greus, M.D., Badia-Valiente, J.D., Teruel-Juanes, R., Gil-Castell, O., Bosio, B., Arato, E., 2021 February 24. Procedimiento de adsorción de nitratos mediante sílice modificada activa a partir de ceniza de paja de arroz. Spain patent ES2727673 B2.
- Radnia, H., Ghoreyshi, A.A., Younesi, H., Masomi, M., Pirzadeh, K., 2013. Adsorption of Fe (II) from aqueous phase by chitosan: application of physical models and artificial neural network for prediction of breakthrough. *Int. J. Eng. Trans. B Appl.* 26, 845–858.
- Singh, A.K., 2016. Nanoparticle ecotoxicology. *Engineered Nanoparticles* <https://doi.org/10.1016/b978-0-12-801406-6.00008-x>.
- Šoltys, M., Balouch, M., Kašpar, O., Lhotka, M., Ulbrich, P., Zadražil, A., Kovačik, P., Štěpánek, F., 2018. Evaluation of scale-up strategies for the batch synthesis of dense and hollow mesoporous silica microspheres. *Chem. Eng. J.* 334, 1135–1147.
- Sulyman, M., Namiesnik, J., Gierak, A., 2017. Low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: a review. *Polish J. Environ. Stud.* 26, 479–510.
- Sun, Y., Yanagisawa, M., Kunimoto, M., Nakamura, M., Homma, T., 2017. Depth profiling of APTES self-assembled monolayers using surface-enhanced confocal Raman microspectroscopy. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 184, 1–6.
- Suzaimi, N.D., Goh, P.S., Malek, N.A.N.N., Lim, J.W., Ismail, A.F., 2019. Performance of branched polyethyleneimine grafted porous rice husk silica in treating nitrate-rich wastewater via adsorption. *J. Environ. Chem. Eng.* 7, 103235.
- Tanev, P.T., Pinnavaia, T.J., 1996. Mesoporous silica molecular sieves prepared by ionic and neutral surfactant templating: a comparison of physical properties. *Chem. Mater.* 8, 2068–2079.
- Vaish, B., Srivastava, V., Kumar Singh, P., Singh, P., Pratap Singh, R., 2019. Energy and nutrient recovery from agro-wastes: rethinking their potential possibilities. *Environ. Eng. Res.* 25, 623–637.
- Wollin, K.M., Dieter, H.H., 2005. Toxicological guidelines for monocyclic nitro-, amino- and aminonitroaromatics, nitramines, and nitrate esters in drinking water. *Arch. Environ. Contam. Toxicol.* 49, 18–26.
- Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G.H., Chmelka, B.F., Stucky, G.D., 1998. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 Angstrom pores. *Science* (80) 279, 548 LP–552 LP.