

Alternative use of rice straw ash as natural fertilizer to reduce phosphorus pollution in protected wetland ecosystems

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Abstract

Purpose The uncontrolled discharge of phosphorus into aquatic environment leads to the deterioration of the water bodies. Additionally, the agricultural crops present inside the La Albufera de Valencia Natural Park, rice fields mainly, have a high social and environmental value. However, there is a conflict between private interests (farmers) and public interest in the management of agro-waste produced by them. Nowadays, the option used by the farmers is the uncontrolled burning in the own field. The ashes generated during the combustion process could be used to remove phosphorus loading in water bodies of the Natural Park, contributing to its recovery.

Methods Adsorption experiments were carried out in batch mode by using different concentrations (5-100 mgP L⁻¹) of sodium phosphate dibasic (Na₂HPO₄) placed in 100 mL stoppered conical flask with 50 mL of synthetic wastewater and different amounts of adsorbent, during the selected time (5 days). Adsorption studies were performed with doses varying from 5 to 24 g L⁻¹. After finishing the adsorption experiments, the solution was filtered through glass microfiber filter (1.2 µm).

Results The adsorption capacity varies for rice straw ash from 31.91% up to 97.48% and rice straw ash with HCl from 17.49% up to 89.04%. An increase in temperature or dosage had a positive effect in the removal capacity, increasing its adsorption. Removal process of phosphorus was endothermic.

Conclusion The use of rice straw ash could be a solution to reduce the phosphate in water bodies, providing an advantage to the proposed alternative of agro-waste management.

Keywords Adsorption isotherms, Agro-waste, Circular economy, Phosphate removal, Rice straw ash

Introduction

The Mediterranean Sea has 2,510,000 km² of water surface area and a coastline length of 46,000 km. The coast of the Mediterranean Sea has about 400 coast lagoons covering an area of 640,000 ha. These coast lagoons are very different in their surface ranging

from 2 up to 78,000 ha. These singular ecosystems are suffering from drainage and pollution processes since the 19th century (Webb 2008). It is estimated that around 60% of Spanish natural wetlands have disappeared in the last 40 years. Also, in other countries such as Italy, natural wetlands have decrease of 73,000 to 13,000 ha during the last century (Cataudella et al. 2015).

At the same time, in the Mediterranean countries in Europe, Africa and Asia, the total rice production area is 1,964,000 ha, and the most important countries are Egypt (680,000 ha), Italy (224,000 ha) and Spain (117,000 ha) (Longoni 2010).

During the second half of the 20th century, the water quality of the lagoons was deteriorated due to the urban and industrial growth and the agricultural practices around the natural wetlands (Soria 2006). Nowadays, these natural wetlands are a hypereutrophic system with predominance of cyanophytes, lack of zooplankton and absence of submerged vegetation (Martín et al. 2013).

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The Natural Park La Albufera de Valencia in Spain is one of the most important natural wetlands in Europe. It has around 15,000 ha of rice fields and produces around 80,000 tons of rice straw per year. Since 1990, the Natural Park is included in the Ramsar List (Ramsar Convention). Since 1991, it is considered a Special Protection Area (SPA) under the European Union Directive on the Conservation of Wild Birds (EU Directive 2009/147/EC) and is included in the network Natura 2000. Furthermore, it has been defined as a heavily modified water body by the European Water Framework Directive (EU Directive 2000/60/EC). Consequently, it is necessary to carry out actions to reduce both external and internal loads of nutrients, mainly nitrogen and phosphorus (He et al. 2016; Martín et al. 2013).

In the coast lagoons, the production of rice crops is very important for the sustainable maintenance of these anthropogenic ecosystems, making a good balance possible between positive environmental impacts (mainly landscape, water quality and biodiversity of flora and fauna), economic income for farmers and maintenance of cultural values of the region. Additionally, the rice fields produce positive environmental impacts, as these become an integral element of providing natural wetland refuge for migratory birds during the winter (Fasola and Ruiz 1996; Hulshof and Vos 2016; López-Pomares et al. 2015).

However, rice straw is one of the most difficult materials to manage nowadays (A Dobermann and Fairhurst 2002), especially in natural environments with high ecological value, as natural wetlands are. Traditionally, since these rice waste stopped having economic value, burning the straw in the own field has been their main management (Sanchis et al. 2014). Farmers consider that this practice favours the destruction of fungal spores, as well as some bacteria and seeds of weeds, facilitating the reincorporation into the soil of certain nutrients (Ribó et al. 2017). However, this practice can produce serious health problems around these areas and considerable environmental damage (Jacobs et al. 1997; Viana et al. 2008), generating a conflict of interest among the nearby inhabitants as well as not being a preferable usage in the EU Common Agricultural Policy (PAC). In line with international trends and EU requirements, multi-stakeholder negotiations are advocated to achieve sustainable development in natural wetlands (Hulshof and Vos 2016).

There are other alternatives for the rice straw management: on the one hand, in situ alternatives

consisting of crushing and soil incorporation, providing organic matter and nutrients (Kongchum et al. 2007), and on the other hand, ex situ alternatives, which involve an extraction of the straw, such as composting, feed for livestock or other biomaterial or bioenergy uses (Guo et al. 2018; Roca-Pérez et al. 2009; Thomas et al. 2016). It should be taken into account that the soil incorporation should be correctly done, otherwise could lead to sulphur toxicity and problems arising from anaerobic decomposition of straw, with an increase in methane emissions. The ex situ alternatives have currently some drawbacks: poor demand of straw, lack of specialized machinery for its extraction and soil nutrient depletion (silica and potassium mainly). For these reasons, farmers show little interest in it (Ribó et al. 2017). Nevertheless, the alternative use as biomass to obtain bioenergy through controlled combustion would reduce impacts associated with air pollution, either by uncontrolled burning in the field or by incorrect soil incorporation of the straw, besides taking advantage of the energetic content of that agro-waste (Hiloidhari and Baruah 2011; Matsumura et al. 2005).

Today, the use of waste is a challenge that society must achieve through research. Thus, the European Union has determined the circular economy as one of the main objectives to achieve, promoting the reuse and recovery of waste by law (EU Directive 2008/98/EC), being "zero waste" the objective of the future waste management systems for solving actual waste problems (Zaman and Lehmann 2013). In this sense, the biomass to energy option could be an attractive alternative in these complex agricultural systems, since the combustion process generates a residue, rice straw ash, rich in minerals that could be used by rice farmers, to reincorporate it in the field, encouraging their interest in this extraction option, apart from its energy value obtained.

"Albufera lagoon shows a phytoplankton bloom in the month of October, as the input loads are determined by the rice cultivation. In April and May, a large number of nutrients arrive at the Albufera from the fertilizers and pesticides used in the preparation of the surrounding rice fields. February and March, on the other hand, present significantly lower chlorophylla concentrations" (Del Barrio et al. 2012). This article shows the concentration of P in the Albufera lagoon that is between 0.49 to 46.38 mgP m⁻² day⁻¹.

Additionally, the bibliography reports the capacity shown by different kinds of ashes to adsorption (Cheung

and Venkitachalam 2000; Lu et al. 2009; Pengthamkeerati et al. 2008; Ugurlu and Salman 1998), but the use of rice straw ash as an adsorbent is not found in bibliography. At the same time, the results corroborate the findings of Abbas (2015) and Karageorgiou (2007), who reported that the product generated after adsorption treatment would have a high fertiliser value in the essential and non-renewable macronutrient for the plant growth, due to its higher phosphorus content (Cordell et al. 2009). Thus, this management alternative could allow reduce the air pollution problems, generate renewable bioenergy from agro-waste and contribute to the recovery of water of lagoons by reducing incoming phosphorus loads and therefore reducing eutrophication. Finally, the adsorbent, enriched with that macronutrient, could be used reincorporating it to the rice fields, based on the “zero waste” objective, and increasing, even more, the farmers’ interest in this management alternative.

Following all these considerations, the principal objective of this research is to assess the adsorption capacity of rice straw ash for the removal of phosphorus from water. In addition, other specific objectives such as batch mode studies were performed to know the influence of different process variables (contact time, pre-treatment of ashes, adsorbent dosage, temperature and effect of ionic strength and calcium cations). Various isotherm models were also tested.

Materials and methods

Collection of materials

Wetlands are complex ecosystems of a great importance for nature conservation (Cherry 2011). The Mediterranean basin has numerous wetlands around lagoons where rice is traditionally grown (Cataudella et al. 2015). These wetlands are normally anthropogenic ecosystems, vital for nature conservation (Hammerl et al. 2004). But they also provide multiple services to neighbouring population, who obtain benefits related to agriculture, landscape, tourism, fishing or flood protection. Nevertheless, wetlands are very fragile and suffer great pressures caused by urban and industrial development (Prigent et al. 2012). The existing biodiversity in these spaces is endangered by the negative impacts they are experiencing (Verones et al. 2013).

As a representative example of these ecosystems, L’Albufera Lagoon is a Natural Park located some 12

km south of Valencia city (Spain). It is a shallow freshwater lagoon with 2,800 ha of surface area, which is separated from the Mediterranean Sea by a large sandbank. The lagoon and surrounding wetlands are a Site of Community Importance (SCI) under the Habitats Directive (EU Directive 92/43/EC) and a Special Protected Area (SPA) under the Birds Directive (EU Directive 2009/147/EC). The lagoon is an important site for birds, particularly wintering and breeding species that use it for resting and nesting. However, despite various levels of protection, the lagoon water fails to meet quality objectives set by the Water Framework Directive (EU Directive 2000/60/EC). Specifically, the lagoon is hypertrophic. It means that there are excess nutrients in the water. This is due to the heavy anthropogenic pressure and intensive agriculture, mainly rice plantations. In an effort to improve water quality, three artificial wetlands – green filters – have been created (in place of rice fields) since 2008. However, improvements are necessary if they effectively support the management requirements of the Natura 2000 network or achieve objectives of the Water Framework Directive. Rice straw (raw material) for the experiment was obtained from rice fields of Lloma de Basarrasa, Cullera (Valencia) (geographical coordinates: 39.209518, -0.248052), inside the Natural Park of L’Albufera. The variety of the cultivated rice is J. Sendra. 15 kg of straw was transported in bags to biomass plant. The rice straw collected in the field has a 20% humidity, in the field it has been packed and without carrying out treatments, the material is introduced into the biomass plant.

Preparation and characterization of adsorbents

The rice straw ash (RSA) was obtained by combustion of raw material in biomass plant and washed thoroughly with deionized water and heated at 823 K for 1 hour in muffle furnace. Then, RSA was sieved with a 1 mm sieve. Acid pre-treatment of RSA using HCl (1 M) was done in order to study the effect of activation of the ashes (Mor et al. 2016). The mixture of HCl and RSA (1:1 v/w ratio) was kept for 24 hours at room conditions (295 K and 45% RH) to prepare rice straw ash with HCl treated (RSA-H). Then, RSA-H was washed with deionized water until neutral pH was obtained in the wash water and later dried at 378 K in the oven.

Characterization of both adsorbents was done using different techniques. To determine the major

and trace elements present in the adsorbent, the chemical analyses were carried out in a Varian 715-ES ICP-Optical Emission spectrometer, after solid dissolution in HNO₃/HCl/HF aqueous solution. Elemental analysis of the ash (C, H, N, S) was performed on a Fisons EA 1108 CHNS-O. To know the crystalline nature of the material, powder X-ray diffraction (PXRD) measurements were performed with a multisample Philips X'Pert diffractometer, equipped with a graphite monochromator operating at 40 kV and 35 mA and using Cu K α radiation ($\lambda = 0.1542$ nm). The particle morphology of the samples was studied by field emission scanning electron microscopy (FESEM), using a ZEISS Ultra5-55 microscope. Furthermore, textural properties were determined by N₂ adsorption-desorption isotherms measured on a Micromeritics ASAP 2020 at 77 K.

The pH at point of zero charge (pH_{PZC}) was determined by the equilibrium technique in a free and controlled ionic strength medium (free and 2.50 mS cm⁻¹ conductivity). The pH of a series of NaCl aqueous solutions have been adjusted using HCl or NaOH aqueous solutions 0.1 M (until the initial pH required, pH_{initial}). Then, pH was again measured (pH_{final}) and the pH_{PZC} was determined through a plot of pH_{initial} versus pH_{final}. The pH varied from pH=2 up to pH=12.

To determine the pH_{PZC}, three experiments were performed for RSA and repeated for RSA-H. The first experiment, samples of adsorbents (~ 500 mg) with NaCl up to 2.50 mS cm⁻¹ conductivity were mixed with 50 mL of each aqueous solution in 100 mL stoppered conical flask and were stirred until reaching equilibrium at 293 K. The second experiment, samples of adsorbents (~ 500 mg) with 10 mg L⁻¹ of Ca and NaCl up to 2.50 mS cm⁻¹ conductivity were mixed with 50 mL in a conical flask of each aqueous solution in 100 mL stoppered conical flask and were stirred until reaching equilibrium at 293 K. The third experiment, samples of adsorbents (~ 500 mg) with 40 mg L⁻¹ of Ca and NaCl up to 2.50 mS cm⁻¹ conductivity were mixed with 50 mL in a conical flask of each aqueous solution in 100 mL stoppered conical flask and were stirred until reaching equilibrium at 293 K.

Batch adsorption experiments

Adsorption experiments were carried out in batch mode by using different concentration (5-100 mgP L⁻¹) of sodium phosphate dibasic (Na₂HPO₄) placed in 100 mL stoppered conical flask with 50 mL of synthetic wastewater and different amounts of

adsorbent, under stirring in a temperature controlled chamber (293 K) during the selected time (120 hours). Adsorption studies were performed with doses varying from 5-24 g L⁻¹. After finishing adsorption experiment, the solution was filtered through glass microfiber filter (1.2 μ m). So, phosphate concentration was determined according to the vanadomolybdophosphoric acid colorimetric method stated by (APHA 2012). Additionally, the filtrate was used to determine pH and electric conductivity.

Adsorption isotherms

Adsorption isotherms show the relation between the total mass adsorbed per gram of adsorbent, q_e (mg g⁻¹), and the equilibrium concentration of adsorbate, C_e (mg L⁻¹), at constant temperature and pH (Tran et al. 2017). Different isotherms have been used to determine the adsorption capacity of adsorbents. Three adsorption models have been used in this research:

a) Langmuir adsorption model (Langmuir 1916): this model assumes that the adsorption process takes place on the surface of the solid in a mono-layer coverage with equivalent sites and without interactions between adsorbate molecules. The Langmuir adsorption model is based on following equation:

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the amount of sorbate at time and equilibrium (mg g⁻¹), q_{max} (mg g⁻¹) is the maximum capacity of adsorption, K_L (L mg⁻¹) is the Langmuir constant that indicates the affinity of the adsorbate for the adsorbent and C_e is the equilibrium concentration of the remaining solute in the solution (mg L⁻¹).

b) Freundlich adsorption model (Freundlich 1906): it is an empirical model based on following equation:

$$q_e = K_F \cdot C_e^{1/n} \quad (2)$$

where K_F (mg^{1-(1/n)} L^{1/n} g⁻¹) is the Freundlich constant that indicates the relative adsorption capacity of the adsorbent and n is a constant that indicates the adsorption intensity.

c) Temkin isotherm model (Temkin 1941): this model assumes that the adsorption heat of all molecules present in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions. Temkin model is based on following equation:

$$q_e = B \ln(K_T \cdot C_e) \quad (3)$$

where K_T ($L\ mg^{-1}$) is the Temkin equilibrium constant and B ($mg\ g^{-1}$) is related with the variation of adsorption energy.

Following (Bolster and Hornberger 2007; Motulsky and Healey 2005), these models have been fitted directly by least squares method (Tran et al. 2017), without any transformation in order to create a linear graph. This avoids violating the assumptions of linear regression (Bolster and Hornberger 2007; Motulsky and Healey 2005). Moreover, following the recommendations of (Tran et al. 2017), the fitting of the models was done by the method of least squares.

Results and discussion

Characterization of adsorbents

The characterization of the different RSA is summarized in Table 1. The main component in the

adsorbents is silicon oxide with a low concentration of other metal oxides as iron, aluminium, copper or zinc. However, the presence of alkaline and alkaline-earth metal oxides is significant (mainly potassium and calcium). This can explain the observed reduction of the basicity of RSA-H compared to RSA. The ashes are essentially inorganic, as observed in the low carbon content. The low value of the surface area, reduced with acid treatment, shows that the adsorbents are not a microporous material. Furthermore, it is expected that most of the adsorbent process take place in the external surface, which represents around 75% of the total area. Moreover, the scanning electron micrograph of the adsorbents (Fig. 1 and supplementary material S1) shows a non-crystalline heterogenic distribution of particles in both materials, with different shapes and sizes, in range from few to a several hundred micrometers.

Table 1 Physical and chemical properties of the adsorbent materials

Samples	RSA	RSA-H
pH _{PZC}	10.1	9.2
BET surface area /($m^2\ g^{-1}$)	12	5
External surface area /(%)	77	72
Elementary analysis /(wt. %)		
C	1.19	-
N	0.00	-
H	0.21	-
S	0.07	-
Composition /(wt. %)		
Si	33.22	33.27
Al	0.74	0.82
Fe	1.07	0.68
Mn	0.06	0.06
Mg	2.82	2.21
Ca	6.66	5.47
Na	1.36	1.22
K	6.39	6.07
P	1.10	1.14
Zn	0.07	0.05
Cu	0.01	0.01

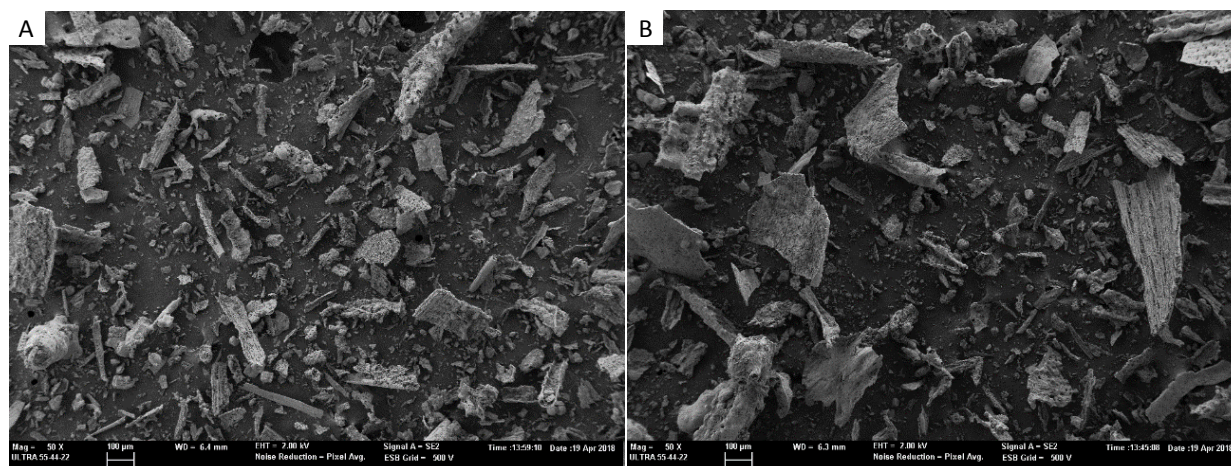


Fig. 1 Scanning electron micrograph of adsorbents: A) RSA and B) RSA-H

Diffraction pattern of the different ashes (Fig. 2) confirmed the low crystallinity of the treated samples as well as the presence of silicon (Si) as the main crystalline phase. The Silicon peaks could indicate the cristobalite phase (Mor et al. 2016). In addition, a relative increase of the signal of Si peaks in the acid-

treated sample can be observed. This fact may be due to the cleaning effect on amorphous soluble species of the adsorbent, increasing the relative crystallinity of the treated solid. Fig. 3 shows the plot used to determine the pH at point of zero charge of both adsorbents (see also Table 1).

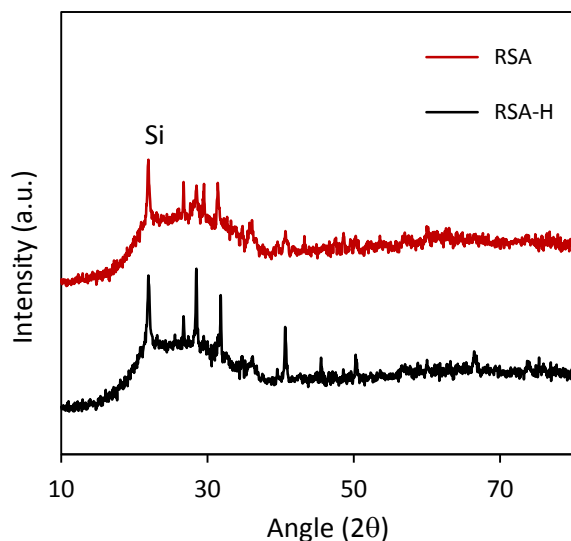


Fig. 2 X-ray diffraction of adsorbents

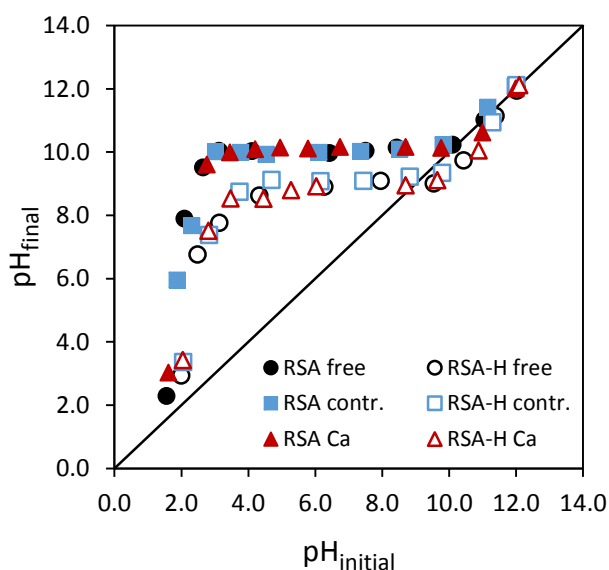


Fig. 3 Determination of the point of zero charge for both adsorbents

The basicity of the samples can be observed (Fig 3) as well as the wide range in which the final pH remains constant regardless of initial pH. This means that the surface behaves as a buffer. The acid treatment has a basicity smoothing effect in the adsorbent, possibly due to the decrease in the content of alkaline-earth oxides. The buffer capacity of both adsorbents does not depend on the ionic strength of the solution (free or controlled conductivity). The presence of calcium in the controlled ionic strength

medium, 40 mg L⁻¹ of calcium from CaCl₂·4H₂O solution in adsorbent Ca captions, did not produce any appreciable effect in neither of the two adsorbents.

Phosphorus adsorption isotherms. Effect of temperature

To study the adsorption isotherms, it is necessary to reach the equilibrium previously (Sircar 2019). The

kinetics of phosphate removal at 283 K, which has been the most unfavourable time for this study, shows that the adsorption process of RSA and RSA-H are

relatively slow and requires at least four days to reach the equilibrium as show Fig. 4.

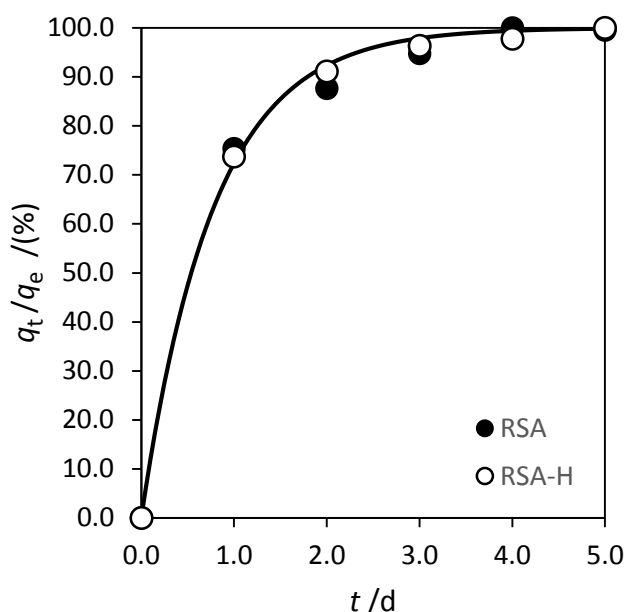


Fig. 4 Kinetics of phosphate removal by both adsorbents at 283 K. Dose of adsorbent, 10 g L⁻¹. Initial phosphate concentration, 60 mgP L⁻¹

Taking it into account, phosphate adsorption isotherms at three different temperatures of RSA (Fig. 5) and RSA-H (Fig. 6) adsorbents were determined, keeping both adsorbent dose (10 g L⁻¹) and pH (10.2 for RSA and 9.4 for RSA-H) constant. The selected temperatures (283 K, 293 K and 303 K) cover the typical annual variation in the water body of the lagoon (Soria 2006). The results in Table 2 clearly show that an increase in temperature leads to an

increase in adsorption capacity for both adsorbents. (Abbas 2015; Mor et al. 2016) describe similar trends.

Table 2, Comparison between adsorbents with their respective Langmuir, Freundlich and Tempkin isotherms in 283, 293 and 303 K according to the Akaike Information Criteria (AIC) and R².

Table 2 Isotherm models for adsorption of phosphate over both materials at different temperatures

Models	T /K	RSA			RSA-H		
		283	293	303	283	293	303
Langmuir	$q_{max} /(\text{mg g}^{-1})$	3.39	4.45	5.24	2.23	2.82	3.22
	$K_L /(\text{L mg}^{-1})$	0.188	0.210	0.220	0.088	0.113	0.151
	R ²	0.95	0.98	0.990	0.97	0.98	0.97
	ΔAIC	0.0					
Freundlich	n	2.82	2.77	2.62	2.43	2.36	2.78
	K_F^*	0.846	1.12	1.31	0.375	0.503	0.737
	R ²	0.87	0.92	0.97	0.92	0.94	0.89
	ΔAIC	95.3					
Tempkin	$B (\text{mg g}^{-1})$	0.726	0.907	1.04	0.503	0.623	0.700
	$K_T (\text{L mg}^{-1})$	1.77	2.31	2.84	0.791	1.07	1.37
	R ²	0.93	0.98	0.994	0.97	0.98	0.96
	ΔAIC	4.8					

* Units of $K_F (\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1})$

Table 2 shows the fitted parameters of the three studied isotherm models, including coefficients of determination (R²). To avoid getting meaningless parameters, all the models have been fitted directly,

without any transformation to create a linear graph (see supplementary material S2), accordingly to (Bolster and Hornberger 2007; Han et al. 2007; Tran et al. 2017, 2015). According to the data obtained,

Freundlich isotherm model can be excluded, since it presents the worst value R^2 in all cases. However, the choice between the remaining two models is complicated, since both show similar R^2 values for each experiment. The lower difference Akaike's Information Criterion (AIC) (Motulsky and Healey 2005) value was obtained with Langmuir isotherm model. Hence, this model is the most probable. Table 2 shows the AIC value between Langmuir and the other isotherm models applied.

Fig. 5 shows the fitted curves obtained for the Langmuir model for RSA and Fig. 6 shows the fitted curves obtained for the Langmuir model for RSA-H. RSA has higher adsorption capacity than RSA-H for all temperatures studied. According to the data shown in Table 2, the variation of q_{max} versus temperature for both adsorbents is represented in Fig 7. This variation is lineal and shows a significantly higher growth rate, almost double, in RSA than in RSA-H adsorbent.

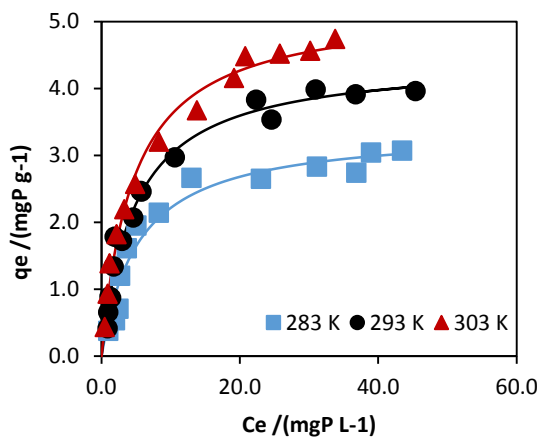


Fig. 5 Phosphate adsorption isotherms at different temperatures for RSA

The theoretical Langmuir model was originally applied to the adsorption of gases on solid surface and, subsequently, to liquid phase. The dynamic equilibrium of adsorption is related to the rate constants of adsorption and desorption. At equilibrium, there is no net change, the sum of these two rates is zero. The constant of this equilibrium (K_L) is the ratio between the adsorption and desorption rate constants. Assuming that (K_L) is essentially an equilibrium constant of the overall process during phosphorus adsorption, its observed temperature dependence can be used to determine the isosteric enthalpy of adsorption ($\Delta_{ad}H^\circ$) using the van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial (1/T)}\right)_\theta = -\frac{\Delta_{ad}H^\circ}{R}$$

Fig. 8 shows the graphical representation of the van't Hoff equation of the experimental data.

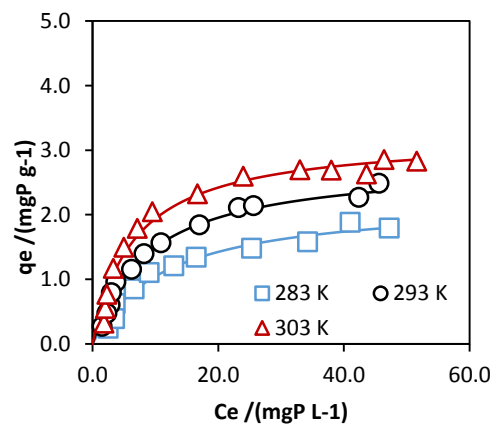


Fig. 6 Phosphate adsorption isotherms at different temperatures for RSA-H

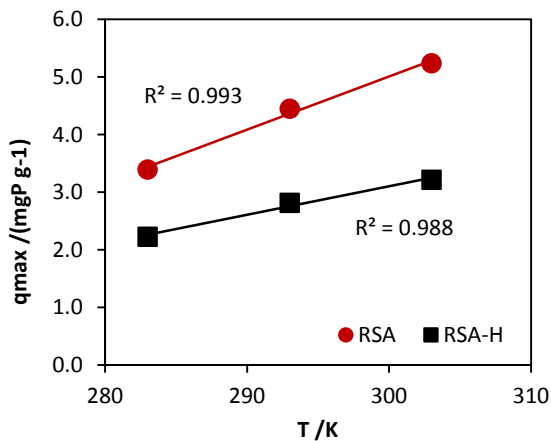


Fig. 7 Effect of temperature on maximum capacity of adsorption

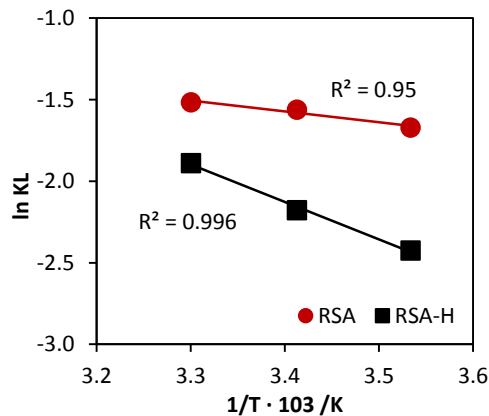


Fig. 8 Effect of temperature on the Langmuir constant

According to equation 4, the slope of each curve represents the isosteric enthalpy of adsorption for each adsorbent. The linearity of the curves is acceptable, as shown by the high values of R^2 . The calculated values of the enthalpy are 5.6 kJ mol^{-1} and 19.1 kJ mol^{-1} for RSA and RSA-H adsorbents, respectively. These positive values indicate the endothermic nature of the global process during the phosphorus removal.

Effect of adsorbent dose

Once again, Langmuir model shows the best results. Fig. 9 shows the effect of dose over the maximum capacity of adsorption of the ashes (q_{max}) obtained by fitting the data to the Langmuir isotherm model. In both cases, it is observed how the increase in the adsorbent dose used has a negative effect on the maximum adsorption capacity, more significantly in the case of RSA adsorbent. In addition, RSA adsorbent continues to have a higher phosphorus adsorption capacity for any dose used.

The pH variation that is observed for increasing doses of adsorbent (10.1-10.4 for RSA and 9.4-9.5 for RSA-H) does not seem to be the main cause for this change in the adsorption capacity. This slight pH variation observed for both adsorbents is in accordance with the results shown in section 3.1, in which it is indicated that the acid treatment has a basicity smoothing effect in the adsorbent, which leads to a lower value and increases in pH with the dose of adsorbent used. However, Fig. 9 shows a significant linear variation of the conductivity, i.e. the concentration of ions in solution, with the dose of adsorbent used. Taking it into account, the reduction in the adsorption capacity can be explained considering the presence of a competitive adsorption between phosphorus and other ions present in the solution by ion exchange or dissolution of part of the adsorbent components, reducing the availability of sites for phosphorus adsorption.

Effect of ionic strength and calcium cations

The higher variation of conductivity with the adsorbent dose of the RSA-H sample and its lower loss of adsorption capacity may seem inconsistent with the results shown in Fig. 9. Therefore, the relative higher conductivity shown by the RSA-H sample could be mainly explained by the presence of chlorides in the solution, coming from the acid

treatment. It can be also additionally explained by the much smaller proportion of other ions coming from the adsorbent, contrary to what happens with the RSA sample.

Fig. 10 shows the effect of ionic strength in the adsorption for RSA adsorbent and Fig. 11 shows the effect of ionic strength in the adsorption for RSA-H adsorbent. The experiments were done at 293 K, an adsorbent dose of 10 g L^{-1} and different concentration of phosphorus in water ($10\text{-}80 \text{ mgP L}^{-1}$). The figures allow comparing the behaviour of the original sample (average conductivity around $630 \mu\text{S cm}^{-1}$ and $770 \mu\text{S cm}^{-1}$ for RSA and RSA-H, respectively) with an experiment with a controlled ionic strength around 2.50 mS cm^{-1} , using the necessary concentration of NaCl. As can be seen, a higher ionic strength, due to the presence of sodium and chloride ions, has a slight positive effect on the adsorption capacity of phosphorus, most significant in the RSA sample. Therefore, the presence of chloride ions does not have any negative effect on the adsorption capacity (Li et al. 2016). In the same way, these ions do not affect the buffer capacity of the adsorbents, as it was seen in section 3.1. This is consistent with the hypothesis raised in the previous section on the effect that the adsorbent dose has on the capacity of phosphorus adsorption. For the RSA-H sample, the main presence of chlorine ions in solution has less effect in reducing the adsorption capacity when the adsorbent dose is increased, even when higher relative conductivities are reached. On the other hand, a higher dose of adsorbent of RSA, not treated with HCl, implies an increase of other ionic species, some of which have a competitive effect on phosphorus adsorption (Afridi et al. 2019).

The slight increase of the adsorption with the presence of sodium and chlorine ions observed in RSA sample (Fig. 10), more sensitive to the adsorbent dose as described in the previous section, may be due to the impediment that supposes a higher ionic strength in the ion exchange/dissolution processes between the solution and the adsorbent (Wu et al. 2019). This impediment would reduce the presence of other competitive ions from the own adsorbent in favour of uncompetitive chlorine ions.

In all cases studied in this research, RSA sample appears as the best material for phosphorus removal. One of the most remarkable chemical property is the reduction of alkaline-earth content (approx. 20% of calcium and magnesium) due to acid treatment. It is

suggested that phosphorus removal depends on the dissolution of calcium ions from the adsorbent and that phosphate fixation is accomplished mainly by these cations (Ahmaruzzaman 2010; Lu et al. 2009; Ugurlu and Salman 1998; Vohla et al. 2011). Therefore, it is expected that the adsorbent with higher calcium content has a greater phosphorus remove capacity, as observed. In order to check the substantive role played by the presence of calcium ions in the dissolution, experiments were done using four different calcium concentrations (10 mg L⁻¹ and 40 mg L⁻¹) from CaCl₂·4H₂O. The tests were done with a controlled ionic strength around 2.50 mS cm⁻¹

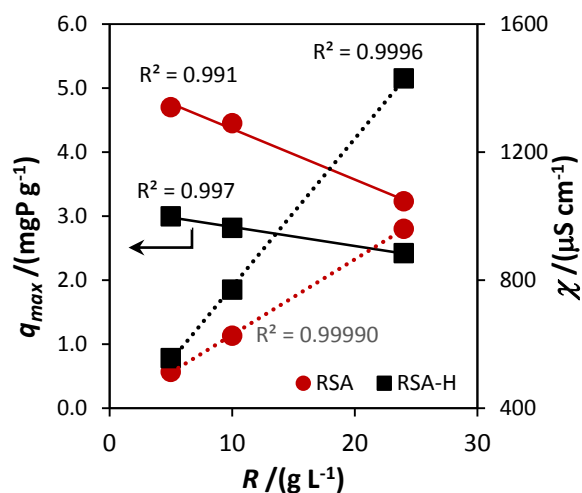


Fig. 9 Effect of adsorbent dose in the maximum capacity of adsorption at 293 K for both adsorbents

at 293 K, an adsorbent dose of 10 g L⁻¹ and different concentration of phosphorus in water, 20-80 mgP L⁻¹. It can be observed that in both cases, the presence of calcium in solution has a positive effect on the phosphorus adsorption capacity. The more increased the capacity, the more concentration there is, confirming the relevance of this cation in the phosphorus removal process. Finally, this explains the best removal behaviour shown by the RSA sample. Fig. 11 shows the results for RSA-H material.

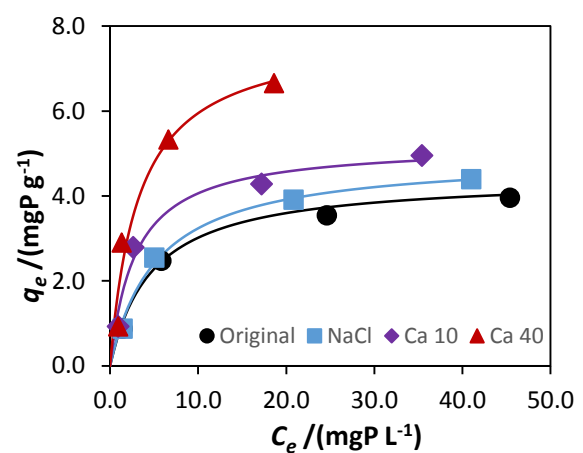


Fig. 10 Effect of ionic strength and calcium in the phosphate removal at 293 K for RSA

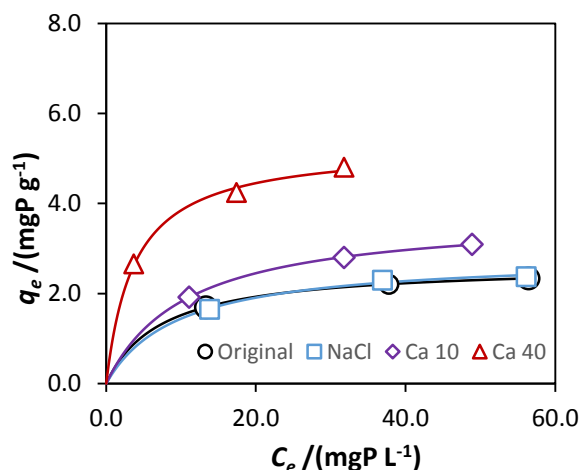


Fig. 11 Effect of ionic strength and calcium in the phosphate removal at 293 K for RSA-H

Conclusions

Based on the results of this research, it is concluded that the rice straw ash removes phosphate from aqueous solution and unlike what happens in other

studies, the acid pre-treatment of the ashes does not improve the remove capacity; then, a simple washing pre-treatment has operative and economic benefits. The differing behaviour between both adsorbents is associated with the content of calcium in the ashes,

lower in the sample treated with acid. The adsorption isotherms of phosphate on both ashes can be well described by Langmuir isotherm model. An increase in temperature has a positive effect in the removal capacity. With the best adsorbent, the maximum adsorption capacity increases with temperature from 3.39 mgP g⁻¹ to 5.24 mgP g⁻¹ in an endothermic removal process. An increase in adsorbent dose has a negative effect on the removal capacity; a competitive adsorption between phosphorus and other ions present in the solution, by ion exchange or dissolution of part of the adsorbent components, takes place. The presence of ions from sodium chloride has no considerable effects on the removal capacity of phosphorus. However, the calcium cations have a relevant effect on it, increasing the removal capacity

with its concentration, confirming the relevance of this cation in the phosphorus removal process.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

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APPENDIX

Supplementary Data – Supporting Information

S1. Scanning electron micrograph of adsorbents

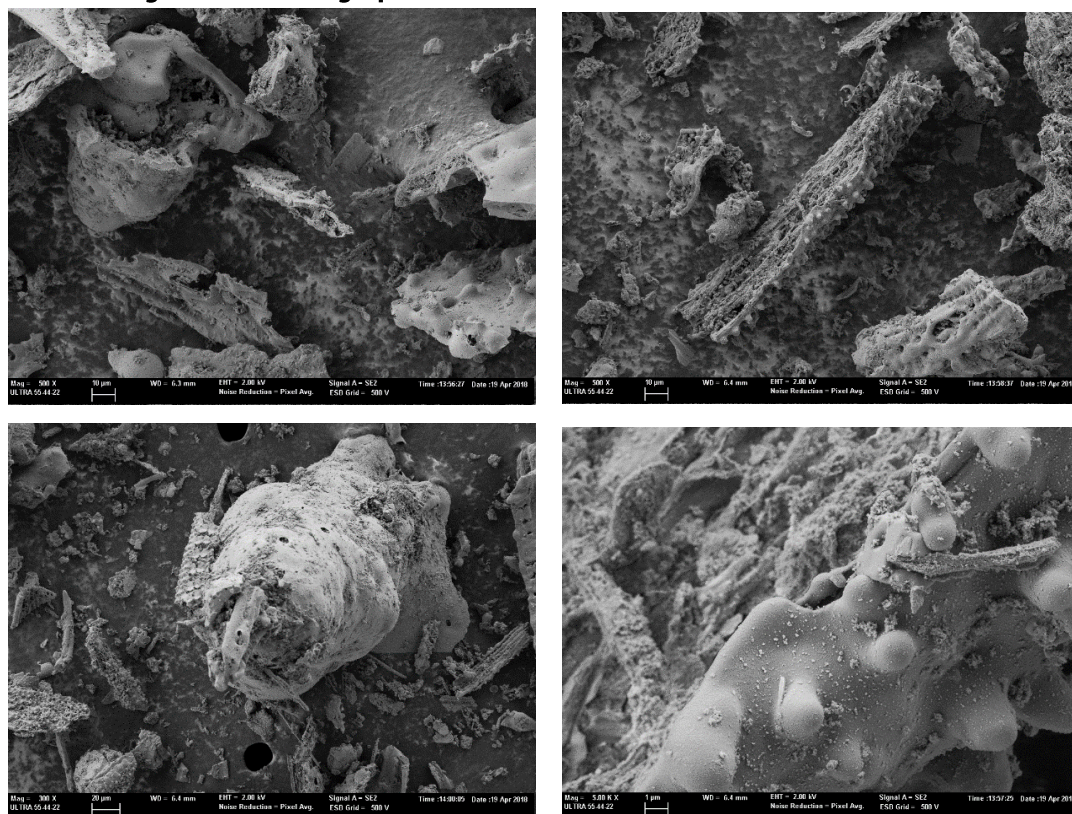


Fig. S1.1. Scanning electron micrograph of RSA adsorbent

S2. Fit of the different linearization of the Langmuir isotherm

$$\text{Non-linearized: } q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

$$\text{Type I: } \frac{C_e}{q_e} = \left(\frac{1}{q_{max}} \right) C_e + \frac{1}{q_{max} K_L}$$

$$\text{Type II: } \frac{q_e}{C_e} = -K_L q_e + q_{max} K_L$$

$$\text{Type III: } \frac{1}{q_e} = \left(\frac{1}{q_{max} K_L} \right) \frac{1}{C_e} + \frac{1}{q_{max}}$$

$$\text{Type IV: } q_e = \left(\frac{-1}{K_L} \right) \frac{q_e}{C_e} + q_{max}$$

$$\text{Type V: } \frac{1}{C_e} = K_L q_{max} \frac{1}{q_e} - K_L$$

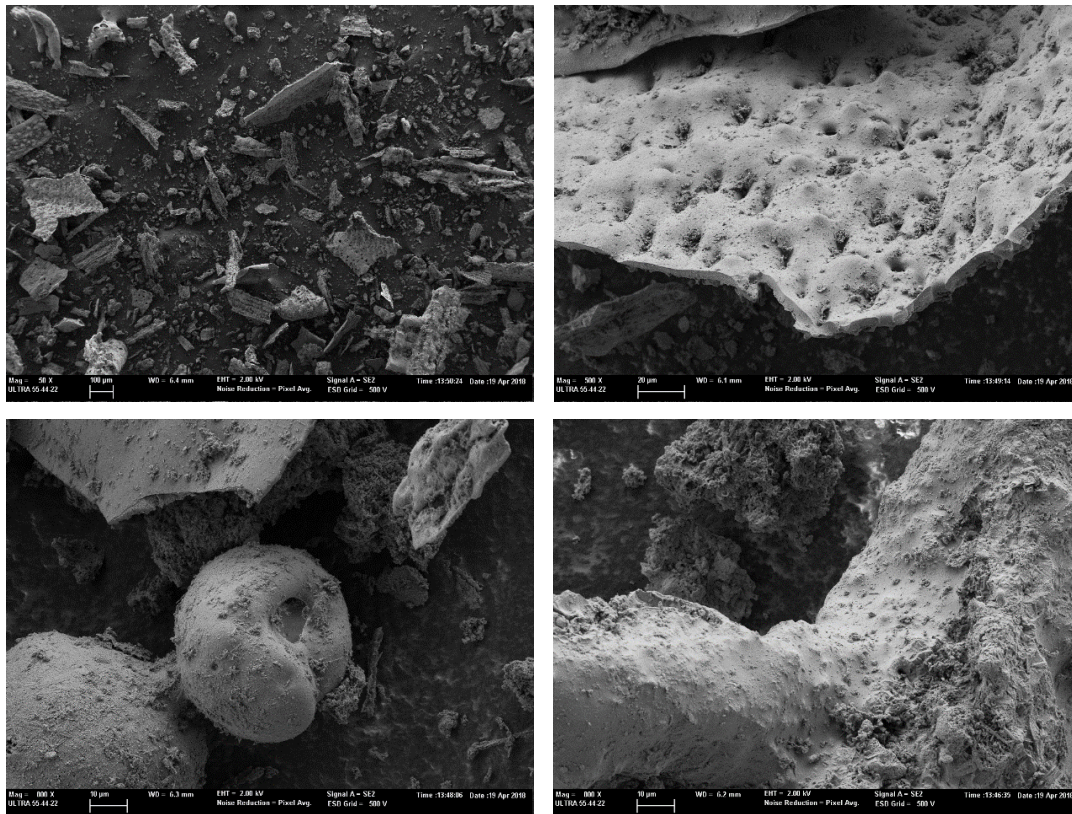


Fig. S1.2. Scanning electron micrograph of RSA-H adsorbent

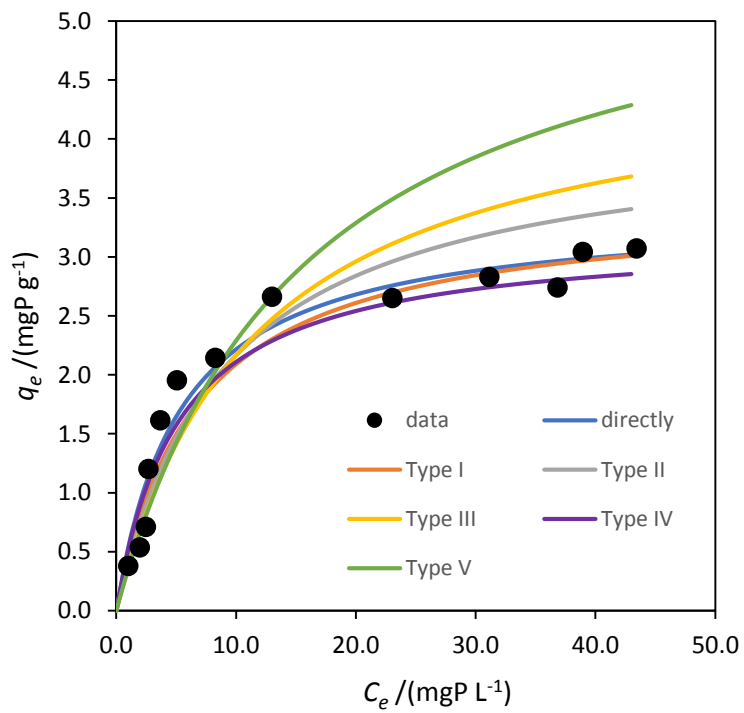


Fig. S3.1. Fit of the different linearization of the Langmuir isotherm over RSA at 283 K. Dose of adsorbent, 10 g L⁻¹

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