UNIVERSITAT
POLITÈCNICA
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PROGRAMA DE DOCTORADO EN INGENIERÍA DEL AGUA Y MEDIOAMBIENTAL

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# UTILIZACIÓN DE RESIDUOS VEGETALES PARA LA ELIMINACIÓN DE FÓSFORO EN AGUAS RESIDUALES MEDIANTE PROCESOS DE ADSORCIÓN

TESIS DOCTORAL

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*Esta tesis está dedicada a mi padre José Carricondo Martínez y a mi hija Martina Carricondo Rodríguez por ser las personas más extraordinarias que he conocido…*

# I.AGRADECIMIENTOS

*Me gustaría expresar mi agradecimiento a los directores de esta investigación, los profesores José Vicente Oliver Villanueva y José Vicente Turégano Pastor, por todos los conocimientos, consejos y por dedicar tiempo y esfuerzo a la preparación de esta tesis.*

*Así mismo me gustaría agradecer a la profesora María Dolores Raigón Jiménez su preciada ayuda en los análisis de materiales.*

# II.RESUMEN

El agua es uno de los elementos más importantes para el desarrollo y supervivencia de los seres vivos. Los primeros asentamientos humanos tuvieron lugar donde el agua era accesible. El ser humano ha ido modificando la forma que ha tenido de relacionarse con las masas de agua dulce, que representan sólo un pequeño porcentaje del total del agua que hay en el planeta. Por ello, resulta primordial para el ser humano y para el resto de los seres vivos gestionar el agua de una forma sostenible.

Además, el desarrollo tecnológico producido a partir de la Revolución Industrial y sobre todo desde el siglo XX ha permitido generar grandes captaciones de agua para abastecimiento humano, así como complejas redes de distribución que aseguran un servicio continuo para los usuarios. No obstante, estos avances no han impedido que todavía hoy se sigan vertiendo grandes cantidades de elementos contaminantes al agua que terminan en el medio natural. Y es que el desarrollo industrial y la aglomeración de la población en entornos urbanos generan focos de contaminación que afectan a las masas de agua próximas, como por ejemplo los humedales, disminuyendo ostensiblemente la calidad del agua. Por ello, resulta fundamental la mejora de la gestión y los tratamientos de depuración de aguas residuales tanto urbanas como industriales.

En este sentido, el 73% de las estaciones depuradoras en España vierten caudales con concentraciones de fósforo superiores a las máximas permitidas por la legislación europea. La Directiva Europea 91/271/CEE sobre tratamiento de las aguas residuales urbanas establece que se pueden verter aguas con una concentración máxima de fósforo de 1 $mg{\cdot}L^{-1}$ en estaciones depuradoras de aguas residuales de más de 100.000 habitantes y de 2 $mg{\cdot}L^{-1}$ en estaciones depuradoras de aguas residuales de

menos de 100.000 habitantes, aunque estos valores están en revisión y cabe esperar su reducción. A la vez que se están vertiendo cantidades de fósforo a las masas de agua a través de las aguas residuales, también se produce contaminación de nitrógeno y fósforo, entre otros, a las aguas subterráneas debido a los lixiviados de los fertilizantes agrícolas.

Los vertidos incontrolados de nitrógeno y fósforo desde plantas de tratamiento de aguas residuales, o en algunos casos vertidos directamente desde zonas urbanas sin haber pasado por una planta de tratamiento, o a partir de lixiviados agrícolas a diferentes masas de agua, han provocado lo que se conoce como eutrofización en ríos, lagos y humedales. La eutrofización se produce cuando hay altas concentraciones de nitrógeno y fósforo en las masas de agua, lo que provoca una gran proliferación de algas, que, una vez que han completado su ciclo vital mueren, generando una biomasa que necesita oxígeno para poder descomponerse. El agua eutrofizada presenta un característico color verdoso y en los casos más extremos, la demanda biológica de oxígeno que requiere esta biomasa en descomposición puede hacer que haya bajas concentraciones de oxígeno en el agua y con ello provocar una degradación de la flora y fauna acuática, incluso su muerte.

Este fenómeno se observa en el lago del Parque Natural de L’Albufera de València, situado al Este de la península Ibérica, y que es uno de los humedales naturales más importantes de la Unión Europea por su valor social, cultural y medioambiental. Este parque natural abarca unas 21.000 hectáreas, de las cuales aproximadamente 14.000 hectáreas están dedicadas al cultivo del arroz. Este cultivo genera alrededor de 85.000 toneladas anuales de paja, lo que representa un residuo de difícil gestión y tratamiento y que tradicional y habitualmente es quemado directamente sobre los campos de cultivo.

El resto de la superficie del parque natural lo ocupa el lago de L'Albufera, donde la especie vegetal mayoritaria es el carrizo, catalogada como especie invasora.

Actualmente, la aplicación de políticas medioambientales ha ido paulatinamente limitando la quema controlada de la paja del arroz, fundamentalmente debido a dos motivos. El primero es el humo que afecta a las poblaciones cercanas, sobre todo en la ciudad como València. Como segundo motivo cabe reseñar el riesgo de propagación de incendios en los ecosistemas forestales colindantes a los campos de cultivo y al lago, a pesar de que las quemas de paja sean controladas por los agricultores. Por la otra parte, el principal motivo por el que los agricultores queman la paja es fundamentalmente económico, ya que el coste de otros tratamientos como la recogida es muy elevado. Otro de los motivos es la creencia de que al quemar este residuo se incrementan las producciones de cereal del siguiente año debido a que el calor del fuego elimina hongos, bacterias e insectos y que los restos de ceniza contienen grandes cantidades de sales minerales que se reincorporan como fertilizantes al suelo. Estas prácticas tradicionales llevadas a cabo por los agricultores del Parque Natural de L'Albufera han sido causa de debate social y científico. Así, por ejemplo, el Instituto Valenciano de Investigaciones Agrarias (IVIA) ha desarrollado estudios de varios años de duración en diferentes parcelas del parque natural comparando tres formas distintas de gestionar el residuo: mediante empacado y extracción de la paja, mediante triturado del residuo en el mismo campo y mediante la quema controlada del residuo. La conclusión es que los rendimientos del cultivo del cereal ($kg \cdot año^{-1}$) no varían. En cualquier caso, la administración autonómica responsable de la gestión del parque ha ido limitando la quema controlada durante los últimos cinco años.

Por otro lado, desde hace siglos se han empleado fertilizantes orgánicos como el estiércol o el guano con el fin de aportar nutrientes al suelo y mejorar su productividad, también en cultivos agrícolas en zonas húmedas como son los arrozales de L'Albufera. Además, con el incremento de las explotaciones agrícolas intensivas, se han sido incorporado mayoritariamente los fertilizantes inorgánicos, como el fósforo procedente de roca mineral. El fósforo, junto con el nitrógeno y el potasio, es uno de los tres macronutrientes que necesita las plantas para poder desarrollarse. Por ello, la Comisión Europea, mediante directivas e informes, recomienda la gestión correcta de todas aquellas materias que se catalogan como materiales críticos, entre las que está el fósforo. También hay recientes investigaciones que pronostican que al ritmo de consumo actual de roca de fósforo, este fertilizante se agotará durante este siglo. Por ello, si no se consigue reducir el consumo y reutilizar el fósforo, se corre el riesgo de que en las próximas décadas no se pueda mantener la agricultura intensiva por la falta de este macronutriente y con ello se vea afectado el actual modelo de agricultura de forma significativa.

Otro de los objetivos estratégicos de la Unión Europea es la mejora de la eficiencia energética y el incremento en el uso de las energías renovables, con el fin de ir consiguiendo una descarbonización progresiva en transición energética como principal herramienta en la mitigación del cambio climático. De hecho, para este año 2020 deberían representar hasta el 20% del total de energía consumida. En este sentido, las plantas de generación de energía eléctrica a partir de la combustión de biomasa representan una alternativa muy eficiente, especialmente si esta biomasa procede de residuos agrícolas. Este es el caso de la planta gestionada por Acciona en Sangüesa (Navarra), que utiliza anualmente 160.000 toneladas de paja de cereal, fundamentalmente de cebada y trigo.

No obstante, el origen de la biomasa para su valorización energética puede ser muy diverso, desde restos de aprovechamientos forestales no maderables, restos de poda de cultivos agrícolas leñosos o no leñosos, fracción verde de los residuos sólidos urbanos, principalmente los restos de los trabajos culturales en los jardines en ciudades, pasando por el material generado en la limpieza y retirada de cañas y carrizos en humedales y ríos, pero también a partir de plantaciones realizadas expresamente para la producción de biomasa, cómo son las de especies de árboles de crecimiento rápido entre las que destacan el chopo, la robinia, el olmo o la paulownia. Esta energía renovable es beneficiosa en diferentes aspectos, ya que genera empleo y riqueza y reutiliza y revaloriza residuos verdes de difícil gestión, contribuyendo a la bioeconomía circular, uno de los objetivos de la Unión Europea. Pero también tiene el inconveniente de que esas plantas de biomasa generan como principal residuo de la combustión la ceniza, que es necesario gestionar adecuadamente.

Por todo ello, la tesis tiene como objetivo general "*analizar y evaluar la posibilidad de utilizar residuos vegetales para la eliminación de fósforo en aguas residuales mediante procesos de adsorción*". Para alcanzar este objetivo general, la tesis persigue los siguientes objetivos específicos:

1. Analizar y evaluar la utilización de la ceniza de la paja de arroz como fertilizante natural reduciendo la contaminación de fósforo en humedales protegidos.

2. Analizar y evaluar la utilización de la ceniza del carrizo (*Phragmites australis*) para el control de la contaminación de fósforo en ecosistemas de humedales antropogénicos.

3. Analizar y evaluar la reducción del fósforo de las aguas residuales a través de procesos de adsorción reutilizando cenizas de madera y paja producidas en instalaciones de bioenergía.

Para su realización, la tesis se ha desarrollado por capítulos, uno para cada uno de los tres objetivos específicos o casos de estudio. El primero se ha centrado en el aprovechamiento de la paja de arroz (*Oryza sativa*) como principal cultivo agrícola del Parque Natural de L'Albufera y principal generador de residuos vegetales, por estar la quema controlada limitada por la actual normativa medioambiental (ver CAPITULO I). El segundo caso de estudio es mediante el uso de carrizo (*Phragmites australis*), que constituye un residuo que se genera en los desbroces de la vegetación invasora del Parque Natural de L'Albufera y que junto con la paja del arroz son los residuos de mayor cantidad del parque natural (ver CAPITULO II).

Por último, se han estudiado las cenizas que provienen directamente de la combustión de diferentes materiales lignocelulósicos en las plantas de generación de energía térmica o cogeneración (energía térmica y eléctrica) de biomasa, como son las cenizas de pajas de otros cereales procedentes de cultivos extensos (por ejemplo, cebada (*Hordeum vulgare L.*) o trigo (*Triticum spp*)) o de madera (por ejemplo de cultivos energéticos de crecimiento rápido como pueden ser los de paulownia (*Paulownia tomentosa*)) (ver CAPITULO III). A su vez, toda la investigación aprovecha el producto que se obtiene de la depuración de las aguas residuales, aportándolo como fertilizante rico en fósforo en parcelas agrícolas en explotación, fundamentalmente en los cultivos de arroz, con el fin de cerrar la valorización de residuos en un concepto de bioeconomía circular.

Para establecer la capacidad de adsorción en el desarrollo metodológico de toda la investigación se determinan el tiempo de contacto entre adsorbente y adsorbato, el pretratamiento de cenizas, la dosificación de adsorbente, la temperatura, el pH y el efecto de la fuerza iónica y los cationes de calcio. Estas determinaciones se realizaron con los modelos de Langmuir, Freundlich y Temkin.

Tras el desarrollo de la fase experimental, los resultados obtenidos demuestran que las diferentes cenizas tienen una importante capacidad de adsorción de fósforo. Así, las cenizas de paja de arroz muestran unas cinéticas de adsorción que llegan al equilibrio a las 96 horas, y alcanzan para la ceniza de paja de arroz un $q_{max}$ de 5,24 $mP \cdot g^{-1}$, mientras para la ceniza de paja de arroz con tratamiento en HCl (1M) llega a un $q_{max}$ de 3,22 $mP \cdot g^{-1}$, ambos adsorbentes a temperaturas de 303 K con una concentración de 10 $gr \cdot L^{-1}$.

Por otra parte, las cenizas de carrizo muestran una cinética de adsorción que llegan al equilibrio a las 72 horas, y que alcanzan un $q_{max}$ que resultó ser de 29,3 $mgP \cdot g^{-1}$ para una concentración de 0,5 $g \cdot L^{-1}$ a 293 K.

Por último, las cenizas de paja de trigo y cebada y las cenizas de madera de paulownia muestran unas cinéticas de adsorción que llegan al equilibrio a las 96 horas, y que alcanzan un $q_{max}$ para la ceniza de paja de trigo de 9,31 $mgP \cdot g^{-1}$ y para la ceniza de paja de cebada de 14,03 $mgP \cdot g^{-1}$, a temperaturas de 303 K con una concentración de 5 $g \cdot L^{-1}$. Por su parte, para la ceniza de madera de paulownia se obtuvo un $q_{max}$ de 15,51 $mgP \cdot g^{-1}$, a temperatura de 303 K y una concentración de 2,5 $g \cdot L^{-1}$.

Con todo ello, tras la evaluación y discusión de los resultados, la investigación desarrollada permite extraer las siguientes conclusiones:

- Las capacidades de eliminación de fósforo para estos materiales varían entre un 20% y más del 90%.

- La isoterma que mejor se ajusta es la de Langmuir. Así, mediante esa isoterma se ha determinado que las cinéticas de adsorción llegan al equilibrio entre 72 horas para el carrizo y 96 horas para el resto de los materiales.

- La fuerza iónica ejercida por los iones de sodio y cloruro o no tiene efectos o tiene un ligero efecto positivo sobre la capacidad de adsorción de fósforo y que una mayor concentración de calcio implica mayor adsorción.

- Estas cenizas poseen un efecto tampón y el uso de HCl (1M) disminuye su capacidad de adsorción.

- El efecto de la dosis del adsorbente hace que varíe la capacidad de adsorción a temperatura constante para todos los tipos de cenizas estudiados.

- Un aumento en la temperatura con entalpia endotérmica influye directamente en un aumento en la capacidad de adsorción para todas las cenizas de todos los materiales estudiados.

- El aporte de estas cenizas puede ser una alternativa como fertilizante natural para los cultivos de arroz en el humedal, contribuyendo a ir sustituyendo a los fertilizantes minerales y mejorando la calidad del agua del lago, con los consiguientes beneficios para la salud de la flora y fauna.

# III.ABSTRACT

Water is one of the most important elements for the development and survival of living things. The first human settlements took place where water was accessible. Human beings have been changing the way they have had to relate to freshwater bodies, which represent only a small percentage of the total water on the planet. Therefore, it is essential for humans and for the rest of living beings that water is managed in a sustainable way.

Furthermore, the technological development produced since the Industrial Revolution, and especially since the 20th century, has allowed the abstraction of large volumes of water for human supply, as well as complex distribution networks that ensure a continuous service for users. However, these advances have not prevented that, even today, large quantities of polluting elements continue to be dumped into the water, ending up in the natural environment. The reason is that industrial development and the agglomeration of the population in urban environments generates sources of contamination that affect nearby water bodies, such as wetlands, ostensibly reducing the quality of the water. Hence, it is essential to improve the management and treatment of both urban and industrial wastewater.

In this respect, 73% of treatment plants in Spain discharge flows with phosphorus concentrations higher than the maximum allowed by European legislation. The European Directive 91/271/EEC on urban wastewater treatment establishes that waters with a maximum phosphorus concentration of 1 mg·L$^{-1}$ can be discharged into wastewater treatment plants with more than 100,000 inhabitants and 2 mg·L$^{-1}$ in wastewater treatment plants of less than 100,000 inhabitants, although these values are under review and a reduction can be expected. While amounts of phosphorus are being dumped into water bodies through wastewater, nitrogen and phosphorus contamination, among

others, also occurs in groundwater due to leachates from agricultural fertilizers.

Uncontrolled discharges of nitrogen and phosphorus from wastewater treatment plants, or in some cases directly discharged from urban areas without having passed through a treatment plant, or from agricultural leachates to different bodies of water, have caused what is known as eutrophication in rivers, lakes and wetlands. Eutrophication occurs when there are high concentrations of nitrogen and phosphorus in water bodies that cause a large proliferation of algae, which, once they have completed their life cycle, die, generating a biomass that needs oxygen to decompose. Eutrophicated water has a characteristic greenish colour and in the most extreme cases, the biological demand for oxygen required by this decomposing biomass can cause low concentrations of oxygen in the water and thereby cause the degradation of aquatic flora and fauna, even their death.

This phenomenon is observed in the lake of the L’Albufera de València Natural Park, located east of the Iberian Peninsula, and which is one of the most important natural wetlands in the European Union due to its social, cultural and environmental value. This natural park covers some 21,000 hectares, of which approximately 14,000 hectares are dedicated to rice cultivation. This crop generates around 85,000 tons of straw per year, which represents a residue that is difficult to manage and treat and which is traditionally and regularly burned directly in the crop fields.

The rest of the surface of the natural park is occupied by the L’Albufera lake, where the main plant species is the reed, classified as an invasive species.

Currently, the application of environmental policies has been gradually limiting the controlled burning of rice straw, mainly for

two reasons. The first is the smoke that affects nearby populations, especially cities such as Valencia. As a second reason, it is worth mentioning the risk of the fires spreading to the forest ecosystems adjacent to the cultivated fields and lake, despite the fact that straw burning is controlled by the farmers. On the other hand, the main reason farmers burn straw is fundamentally economic, since the cost of other treatments, such as its collection, is very high. Another reason is the belief that burning this residue increases cereal production the following year because the heat of the fire eliminates fungi, bacteria and insects and that the ash remains contain large amounts of mineral salts that are reincorporated as fertilizers into the soil. These traditional practices carried out by the farmers of the L'Albufera Natural Park have been the cause of social and scientific debate. Thus, for example, the Valencian Institute for Agricultural Research (IVIA) has carried out studies lasting several years in different plots of the natural park, comparing three different ways of managing the waste: by packing and extracting the straw, by crushing the waste in the same field and by controlled burning of the residue. The conclusion is that the cereal crop yields ($kg \cdot year^{-1}$) do not vary. In any case, the autonomic administration responsible for park management has been limiting the practice of controlled burning for the last five years.

Furthermore, for centuries organic fertilizers such as manure or guano have been used in order to provide nutrients to the soil and improve its productivity, also repeated in agricultural crops in humid areas such as the rice fields of L'Albufera. In addition, with the increase in intensive farming, inorganic fertilizers have been incorporated, such as phosphorus from mineral rock. Phosphorus, along with nitrogen and potassium, is one of the three macronutrients that plants need to develop. For this reason, the European Commission, through directives and reports, recommends the correct management of all those substances that are classified as critical materials, among which is phosphorus.

There is also recent research that predicts that at the current consumption rate of phosphorus rock, this fertilizer will be depleted during this century. For this reason, if it is not possible to reduce consumption and reuse phosphorus, there is a risk that intensive agriculture cannot be maintained in the coming decades due to the lack of this macronutrient and thus the current model of agriculture will be affected significantly.

Another of the strategic objectives of the European Union is to improve energy efficiency and increase the use of renewable energy, in order to gradually achieve a decarbonisation in energy transition as the main tool in mitigating climate change. In fact, by this year 2020 they should represent up to 20% of the total energy consumed. In this sense, electricity generation plants using biomass combustion represent a very efficient alternative, especially if this biomass comes from agricultural residues. This is the case of the plant managed by Acciona in Sangüesa (Navarra), which uses 160,000 tons of cereal straw annually, primarily barley and wheat.

However, the origin of the biomass used for energy recovery can be very diverse, from non-timber forest harvesting remains, pruning remains of woody or non-woody agricultural crops, the green fraction of urban solid waste, mainly the remains of maintenance operations in city gardens, through to the material generated in the cleaning and removal of canes and reeds in wetlands and rivers. The available biomass also includes the plantations grown expressly for this purpose, such as those comprising of fast-growing tree species among which stand out the poplar, the robinia, the elm or the paulownia. This renewable energy is beneficial in different aspects, since it generates employment and wealth, and reuses and revalues difficult to manage green waste, contributing to the circular bioeconomy, one of the objectives of the European Union. But it also has the disadvantage that these biomass plants generate ash as the main combustion residue, which must be properly managed.

For all these reasons, the thesis has the general objective of "analysing and evaluating the possibility of using vegetable residues for the elimination of phosphorus in residual waters through adsorption processes". To achieve this general objective, the thesis pursues the following specific objectives:

1. Analyse and evaluate the use of rice straw ash as a natural fertilizer, reducing phosphorus contamination in protected wetlands.

2. Analyse and evaluate the use of reed ash (*Phragmites australis*) to control phosphorus contamination in anthropogenic wetland ecosystems.

3. Analyse and evaluate the reduction of phosphorus in wastewater through adsorption processes, reusing wood ash and straw ash produced in bioenergy facilities.

In order to attain these, the thesis has been carried out in chapters, one for each of the three specific objectives (or case studies). The first has focused on the use of rice straw (*Oryza sativa*) as it is the main agricultural crop of the L'Albufera Natural Park and the main generator of plant residues, since its controlled burning is being limited by current environmental regulations (see CHAPTER I ). The second case study has used reed ash (*Phragmites australis*), which constitutes a residue that is generated during the clearing of this invasive vegetation from the L'Albufera Natural Park, and which together with the rice straw are the most abundant residues in the natural park (to see CHAPTER II).

Finally, the ashes that come directly from the combustion of different lignocellulosic materials in biomass thermal energy generation or cogeneration (thermal and electrical energy) plants, such as straw ash from other extensively cultivated cereals [for

example, barley (*Hordeum vulgare L.*) or wheat (*Triticum spp*)] or from wood (for example from fast growing energy plantations such as those of Paulownia (*Paulownia tomentosa*)) (see CHAPTER III) have been studied. In turn, all the research has taken advantage of the waste deposits obtained after the purification of wastewater in treatment plants, by employing it as a phosphorus-rich fertilizer in operative agricultural plots, primarily rice crops, in order to recover the waste and so close the loop according to the concept of a circular bioeconomy.

To establish the adsorption capacity in the methodological development of all the research, the contact time between adsorbent and adsorbate, ash pre-treatment, adsorbent dosage, temperature, pH and the effect of ionic strength and cations of calcium are determined. These determinations were achieved using the Langmuir, Freundlich and Temkin models.

After performing the experimental phase, the results obtained show that the different ashes have an important phosphorus adsorption capacity. Thus, rice straw ash shows adsorption kinetics that reach equilibrium at 96 hours, and reach a $q_{max}$ of 5.24 $mP \cdot g^{-1}$, while the rice straw ash treated with HCl (1M) reaches a $q_{max}$ of 3.22 $mP \cdot g^{-1}$, both adsorbents being at a temperature of 303 K with a concentration of 10 $gr \cdot L^{-1}$.

Furthermore, reed ash shows adsorption kinetics that reach equilibrium after 72 hours, and reach a $q_{max}$ that turned out to be 29.3 $mgP \cdot g^{-1}$ for a concentration of 0.5 $g \cdot L^{-1}$ at 293 K.

Lastly, the wheat and barley straw ashes and paulownia wood ash show adsorption kinetics that reach equilibrium at 96 hours, and reach a $q_{max}$ of 9.31 $mgP \cdot g^{-1}$ for wheat straw ash and of 14.03 $mgP \cdot g^{-1}$ for barley straw ash, at temperatures of 303 K with a concentration of 5 $g \cdot L^{-1}$. In addition, for paulownia wood ash, a $q_{max}$ of 15.51 $mgP \cdot g^{-1}$ was obtained, at a temperature of 303 K and a concentration of 2.5 $g \cdot L^{-1}$.

With all this, after evaluating and discussing the results, the research carried out allows the following conclusions to be drawn:

- The phosphorus removal capacities for these materials vary between 20% and more than 90%.
- The best fit isotherm is Langmuir's. Thus, by means of this isotherm it has been determined that the adsorption kinetics reach equilibrium between 72 hours for the reed and 96 hours for the rest of the materials.
- The ionic strength exerted by sodium and chloride ions either has no effect or has a slight positive effect on the capacity of phosphorus adsorption and that a higher concentration of calcium implies greater adsorption.
- These ashes have a buffering effect and the use of HCl (1M) reduces their adsorption capacity.
- The effect of the adsorbent dose causes the adsorption capacity to vary at constant temperature for all types of ash studied.
- An increase in temperature with endothermic enthalpy directly influences an increase in the adsorption capacity for all the ashes of all the materials studied.
- The contribution of these phosphorus enriched ashes can be as an alternative natural fertilizer for rice crops in the wetland, helping to replace mineral fertilizers and improving the quality of the lake water, with the consequent benefits for the health of the flora and wildlife.

# IV.RESUM

L'aigua és un dels elements més importants per al desenvolupament i la supervivència dels éssers vius. Els primers assentaments humans van tenir lloc on l'aigua era accessible. L'ésser humà ha anat modificant la forma que ha tingut de relacionar-se amb les masses d'aigua dolça, que representen només un xicotet percentatge del total de l'aigua que hi ha en el planeta. Per això, resulta primordial per a l'ésser humà i per a la resta dels éssers vius gestionar l'aigua d'una forma sostenible.

A més, el desenvolupament tecnològic produït a partir de la revolució industrial, sobretot des del segle XX, ha permès generar grans captacions d'aigua per al proveïment humà, així com complexes xarxes de distribució que asseguren un servei continu per a les persones usuàries. No obstant això, aquests avanços no han impedit que encara avui dia es continuen abocant grans quantitats d'elements contaminants a l'aigua, que acaben en el medi natural. I és que el desenvolupament industrial i l'aglomeració de la població en entorns urbans generen focus de contaminació que afecten les masses d'aigua pròximes, com per exemple els aiguamolls, i que disminueixen ostensiblement la qualitat de l'aigua. Per això, resulta fonamental la millora de la gestió i els tractaments de depuració d'aigües residuals, tant urbanes com industrials.

En aquest sentit, el 73% de les estacions depuradores a Espanya aboquen cabals amb concentracions de fòsfor superiors a les màximes permeses per la legislació europea. La Directiva europea 91/271/CEE sobre tractament de les aigües residuals urbanes estableix que es poden abocar aigües amb una concentració màxima de fòsfor de 1 $mg{\cdot}L^{-1}$ en estacions depuradores d'aigües residuals de més de 100.000 habitants i de 2 $mg{\cdot}L^{-1}$ en estacions depuradores d'aigües residuals de menys de 100.000 habitants, encara que aquests valors estan revisant-se i cal esperar la seua

reducció. Alhora que s'estan abocant quantitats de fòsfor a les masses d'aigua a través de les aigües residuals, també es produeix contaminació de nitrogen i fòsfor, entre altres, a les aigües subterrànies, a causa dels lixiviats dels fertilitzants agrícoles.

Els abocaments incontrolats de nitrogen i fòsfor des de plantes de tractament d'aigües residuals, o en alguns casos abocats directament des de zones urbanes sense haver passat per una planta de tractament, o a partir de lixiviats agrícoles a diferents masses d'aigua, han provocat el que es coneix com eutrofització en rius, llacs i aiguamolls. L'eutrofització es produeix quan hi ha altes concentracions de nitrogen i fòsfor en les masses d'aigua, la qual cosa provoca una gran proliferació d'algues, que, una vegada que han completat el seu cicle vital, moren i generen una biomassa que necessita oxigen per a poder descompondre's. L'aigua eutrofitzada presenta un característic color verdós i, en els casos més extrems, la demanda biològica d'oxigen que requereix aquesta biomassa en descomposició pot fer que hi haja baixes concentracions d'oxigen en l'aigua i, amb això, pot provocar una degradació de la flora i fauna aquàtica, fins i tot la seua mort.

Aquest fenomen s'observa al llac del Parc Natural de l’Albufera de València, situat a l'est de la península Ibèrica, i que és un dels aiguamolls naturals més importants de la Unió Europea pel valor social, cultural i mediambiental. Aquest parc natural abasta unes 21.000 hectàrees, de les quals aproximadament 14.000 estan dedicades al cultiu de l'arròs. Aquest cultiu genera al voltant de 85.000 tones anuals de palla, la qual cosa representa un residu de difícil gestió i tractament, i que tradicionalment i habitualment és cremat directament sobre els camps de cultiu.

La resta de la superfície del parc natural l'ocupa el llac de l’Albufera, on l'espècie vegetal majoritària és el canyís o senill, catalogada com a espècie invasora.

Actualment, l'aplicació de polítiques mediambientals ha anat limitant gradualment la crema controlada de la palla de l'arròs, fonamentalment a causa de dos motius. El primer és el fum que afecta les poblacions pròximes, sobretot la ciutat de València. Com a segon motiu cal ressenyar el risc de propagació d'incendis als ecosistemes forestals confrontants als camps de cultiu i al llac, a pesar que les cremes de palla siguen controlades pels agricultors. D’altra banda, el principal motiu pel qual els agricultors cremen la palla és fonamentalment econòmic, ja que el cost d'altres tractaments com la recollida és molt elevat. Un altre dels motius és la creença que en cremar aquest residu s'incrementen les produccions de cereal de l’any següent pel fet que la calor del foc elimina fongs, bacteris i insectes, i que les restes de cendra contenen grans quantitats de sals minerals que es reincorporen com a fertilitzants al sòl. Aquestes pràctiques tradicionals dutes a terme pels agricultors del Parc Natural de l’Albufera han sigut causa de debat social i científic. Així, per exemple, l'Institut Valencià d'Investigacions Agràries (IVIA) ha desenvolupat estudis d’uns quants anys de duració en diferents parcel·les del parc natural, comparant tres formes diferents de gestionar el residu: mitjançant empacament i extracció de la palla; mitjançant trituració del residu al mateix camp, i mitjançant la crema controlada del residu. La conclusió és que els rendiments del cultiu del cereal (kg/any$^{-1}$) no varien. En qualsevol cas, l'administració autonòmica responsable de la gestió del parc ha anat limitant la crema controlada durant els últims cinc anys.

D'altra banda, des de fa segles s'han emprat fertilitzants orgànics com el fem o el guano amb la finalitat d'aportar nutrients al sòl per millorar-ne la productivitat, també en cultius agrícoles de zones humides com ho són els arrossars de l’Albufera. A més, amb l'increment de les explotacions agrícoles intensives, s'han anat incorporant majoritàriament els fertilitzants inorgànics, com el fòsfor procedent de roca mineral. El fòsfor, juntament amb el nitrogen i el potassi, és un dels tres macronutrients que necessiten les plantes per a poder desenvolupar-se. Per això, la Comissió Europea, mitjançant directives i informes, recomana la gestió correcta de totes aquelles matèries que es cataloguen com materials crítics, entre les quals es troba el fòsfor. També hi ha investigacions recents que pronostiquen que al ritme de consum actual de roca de fòsfor, aquest fertilitzant s'esgotarà durant aquest segle. Per això, si no s'aconsegueix reduir el consum i reutilitzar el fòsfor, es corre el risc que en les pròximes dècades no es puga mantenir l'agricultura intensiva per la falta d'aquest macronutrient i, amb això, que es veja afectat l'actual model d'agricultura de manera significativa.

Un altre dels objectius estratègics de la Unió Europea és la millora de l'eficiència energètica i l'increment en l'ús de les energies renovables, amb la finalitat d'anar assolint una descarbonització progressiva en transició energètica com a principal eina en la mitigació del canvi climàtic. De fet, per a aquest any 2020 haurien de representar fins el 20% del total de l'energia consumida. En aquest sentit, les plantes de generació d'energia elèctrica a partir de la combustió de biomassa representen una alternativa molt eficient, especialment si aquesta biomassa procedeix de residus agrícoles. Aquest és el cas de la planta gestionada per Acciona a Sangüesa (Navarra), que utilitza anualment 160.000 tones de palla de cereal, fonamentalment d'ordi i blat.

No obstant això, l'origen de la biomassa per a la seua valorització energètica pot ser molt divers, des de restes d'aprofitaments forestals no fusters, restes de poda de cultius agrícoles llenyosos o no llenyosos, fracció verda dels residus sòlids urbans, principalment les restes dels treballs culturals als jardins de les ciutats, passant pel material generat en la neteja i retirada de canyes i senill en aiguamolls i rius, però també a partir de plantacions realitzades expressament per a la producció de biomassa, com ara les d'espècies d'arbres de creixement ràpid, entre les quals destaquen el xop, la robínia, l'om o la paulònia.

Aquesta energia renovable és beneficiosa en diferents aspectes, ja que genera ocupació i riquesa, i reutilitza i revaloritza residus verds de difícil gestió, contribuint a la bioeconomia circular, un dels objectius de la Unió Europea. Però també té l'inconvenient que aquestes plantes de biomassa generen com a principal residu de la combustió la cendra, que és necessari gestionar adequadament.

Per tot això, la tesi té com a objectiu general: “analitzar i avaluar la possibilitat d'utilitzar residus vegetals per a l'eliminació de fòsfor en aigües residuals mitjançant processos d'adsorció”. Per a aconseguir aquest objectiu general, la tesi persegueix els objectius específics següents:

1. Analitzar i avaluar la utilització de la cendra de la palla d'arròs com a fertilitzant natural que redueix la contaminació de fòsfor en aiguamolls protegits.

2. Analitzar i avaluar la utilització de la cendra del canyís (*Phragmites australis*) per al control de la contaminació de fòsfor als ecosistemes d'aiguamolls antropogènics.

3. Analitzar i avaluar la reducció del fòsfor de les aigües residuals a través de processos d'adsorció reutilitzant cendres de fusta i palla produïdes en instal·lacions de bioenergia.

Per a realitzar-la, la tesi s'ha desenvolupat per capítols, un per a cadascun dels tres objectius específics o casos d'estudi. El primer s'ha centrat en l'aprofitament de la palla d'arròs (*Oryza sativa*) com a principal cultiu agrícola del Parc Natural de l’Albufera i principal generador de residus vegetals, per estar la crema controlada limitada per l'actual normativa mediambiental (vegeu el CAPÍTOL I). El segon cas d'estudi és mitjançant l'ús del canyís o senill (*Phragmites australis*), que constitueix un residu que es genera en els desbrossaments de la vegetació invasora del Parc Natural de l’Albufera i que, juntament amb la palla de l'arròs, són els residus més abundants del parc natural (vegeu el CAPÍTOL II).

Finalment, s´han estudiat les cendres que provenen directament de la combustió de diferents materials lignocel·lulòsics a les plantes de generació d'energia tèrmica o cogeneració (energia tèrmica i elèctrica) de biomassa, com les cendres de palles d'altres cereals procedents de cultius extensos [per exemple, ordi (*Hordeum vulgare L.*) o blat (*Triticum spp*)] o de fusta [per exemple, de cultius energètics de creixement ràpid com els de paulònia (*Paulownia tomentosa*)] (vegeu el CAPÍTOL III). Al seu torn, tota la investigació aprofita el producte que s'obté de la depuració de les aigües residuals, aportant-lo com a fertilitzant ric en fòsfor en parcel·les agrícoles en explotació, fonamentalment als cultius d'arròs, amb la finalitat de tancar la valorització de residus en un concepte de bioeconomia circular.

Per a establir la capacitat d'adsorció en el desenvolupament metodològic de tota la investigació es determinen els temps de contacte entre adsorbent i adsorbat, el pretractament de cendres, el dosatge d'adsorbent, la temperatura, el pH i l'efecte de la força iònica i els cations de calci. Aquestes determinacions es van realitzar amb els models de Langmuir, Freundlich i Temkin.

Després del desenvolupament de la fase experimental, els resultats obtinguts demostren que les diferents cendres tenen una important capacitat d'adsorció de fòsfor. Així, les cendres de palla d'arròs mostren unes cinètiques d'adsorció que arriben a l'equilibri a les 96 hores, i assoleixen per a la cendra de palla d'arròs un qmax de 5,24 $mP \cdot g^{-1}$, mentre que per a la cendra de palla d'arròs amb tractament en HCl (1M) arriba a un qmax de 3,22 $mP \cdot g^{-1}$, tots dos adsorbents a temperatures de 303 K amb una concentració de 10 $gr \cdot L^{-1}$.

D'altra banda, les cendres de senill mostren una cinètica d'adsorció que arriba a l'equilibri a les 72 hores, i que assoleix un qmax que ha resultat ser de 29,3 mgP·g$^{-1}$ per a una concentració de 0,5 g·L$^{-1}$ a 293 K.

Finalment, les cendres de palla de blat i ordi i les cendres de fusta de paulònia mostren unes cinètiques d'adsorció que arriben a l'equilibri a les 96 hores, i que assoleixen un qmax per a la cendra de palla de blat de 9,31 mgP·g$^{-1}$ i per a la cendra de palla d'ordi de 14,03 mgP·g$^{-1}$, a temperatures de 303 K amb una concentració de 5 g·L$^{-1}$. Per part seua, per a la cendra de fusta de paulònia es va obtenir un qmax de 15,51 mgP·g$^{-1}$, a temperatura de 303 K i una concentració de 2,5 g·L$^{-1}$.

Amb tot això, després de l'avaluació i discussió dels resultats, la investigació desenvolupada permet extraure les conclusions següents:

- Les capacitats d'eliminació de fòsfor per a aquests materials varien entre un 20% i més del 90%.

- La isoterma que millor s'ajusta és la de Langmuir. Així, mitjançant aquesta isoterma s'ha determinat que les cinètiques d'adsorció arriben a l'equilibri entre les 72 hores del senill i les 96 hores de la resta dels materials.

- La força iònica exercida pels ions de sodi i clorur, o bé no té efectes o bé té un lleuger efecte positiu sobre la capacitat d'adsorció de fòsfor, i una major concentració de calci implica una major adsorció.
- Aquestes cendres tenen un efecte tampó i l'ús de HCl (1M) disminueix la seua capacitat d'adsorció.

- L'efecte de la dosi de l'adsorbent fa que varie la capacitat d'adsorció a temperatura constant per a tots els tipus de cendres estudiats.

- Un augment en la temperatura amb entalpia endotèrmica influeix directament en un augment en la capacitat d'adsorció per a totes les cendres de tots els materials estudiats.

- L'aportació d'aquestes cendres pot ser una alternativa com a fertilitzant natural per als cultius d'arròs a l'aiguamoll, que contribueix a la substitució dels fertilitzants minerals i a la millora de la qualitat de l'aigua del llac, amb els consegüents beneficis per a la salut de la flora i fauna.

# V.CONTENIDOS

# VI.LISTA DE FIGURAS

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# VIII. LISTA UNIDADES Y ABREVIATURAS

**1M:** 1 Molar

**$\Delta adH^{o}$**: entalpia de adsorción

**AIC**: criterio de información de Akaike

$B$: variación de la energía de adsorción de Tempkin

**BSA**: ceniza de paja de cebada

**$C_e$**: concentración en equilibrio

**$C_F$**: concentración final

**$C_o$**: concentración inicial

**g:** gramo

**ha:** hectáreas

**K:** grados Kelvin

**$K_F$**: constante de Freundlich

**Kg:** kilogramo

**kJ**: kilojulio

**$K_L$**: constante de Langmuir

**km:** kilómetros

$K_T$: Constante de equilibrio de Tempkin

**kV:** kilovoltio

**L:** litro

$ln\,K$: Logaritmo neperiano de la constante de equilibrio

**m:** metro

**mA:** miliamperio

**mg:** miligramo

**mgP:** miligramo de fósforo

**MJ**: Megajulio

**mL**: mililitro

**mm**: milímetro

**mol**: mol

**mS cm**$^{-1}$: microsiemens por centímetro

**n**: constante de adsorción de Freundlich

**nm:** nanómetro

$\theta$: fracción de recubrimiento

**ppm**: partes por millón

**PWA**: ceniza de paja de paulonia

$q_{max}$**:** Capacidad máxima de adsorción

**R**: constante de gases ideales

**RA**: ceniza de carrizo

**RSA**: ceniza de paja de arroz

**RSA-H:** ceniza de paja de arroz con tratamiento de HCl

**SEM**: micrografía electrónica de barrido

**t:** tonelada

**T**: Temperatura

**µm**: micrómetro

**µS cm**$^{-1}$: decisiemens por centímetro

**V**: volumen

**W**: peso

**WSA**: ceniza de paja de trigo

**wt. %**: Porcentaje en peso

# 1.INTRODUCCIÓN

## 1.1 Motivación de la investigación

La principal motivación para realizar esta investigación es el interés del autor en los problemas medioambientales del Parque Natural de L´Albufera de València, concretamente en el problema derivado de los vertidos al lago a través de las aguas residuales urbanas (Santamarta *et al.*, 2014), y por los lixiviados de los fertilizantes agrícolas (García-Nieto *et al.*, 2016).

Se debe de tener en cuenta que para el tratamiento de fósforo no se ha encontrado una solución técnica que sea de bajo coste, buena eficiencia y que además consiga mejorar diferentes problemáticas dentro de humedales (Soria, 2006). En esta tesis se plantea el uso de diferentes residuos vegetales como adsorbentes para la depuración de agua residuales mediante la eliminación de fósforo, teniendo en cuenta que los procesos de adsorción pueden ser una metodología apta que puede contribuir a solucionar parcialmente los problemas de contaminación del humedal en el Parque Natural de L´Albufera de València.

El Parque Natural de L´Albufera de València se encuentra situado a 10 km al sur de Valencia, tiene una superficie de 21.120 ha (ver Figura 1) y fue declarado Parque Natural el 8 de julio de 1986 por la Generalitat Valenciana. Desde el punto de vista medioambiental es importante por albergar una gran variedad de especies vegetales y animales; en cuanto a la fauna piscícola el parque natural alberga gran variedad de especies, algunas de ellas protegidas como el fartet (*Aphanius Iberus*) o el samaruc (*Valencia hispánica*).

También cabe destacar su importancia cultural y económica debido a actividades como el cultivo tradicional del arroz, la gastronomía al ser la cuna de la paella valenciana como plato fundamental del patrimonio gastronómico español, el turismo cultural y de playa, la actividad deportiva en la naturaleza donde destaca la vela latina, la pesca y la caza.

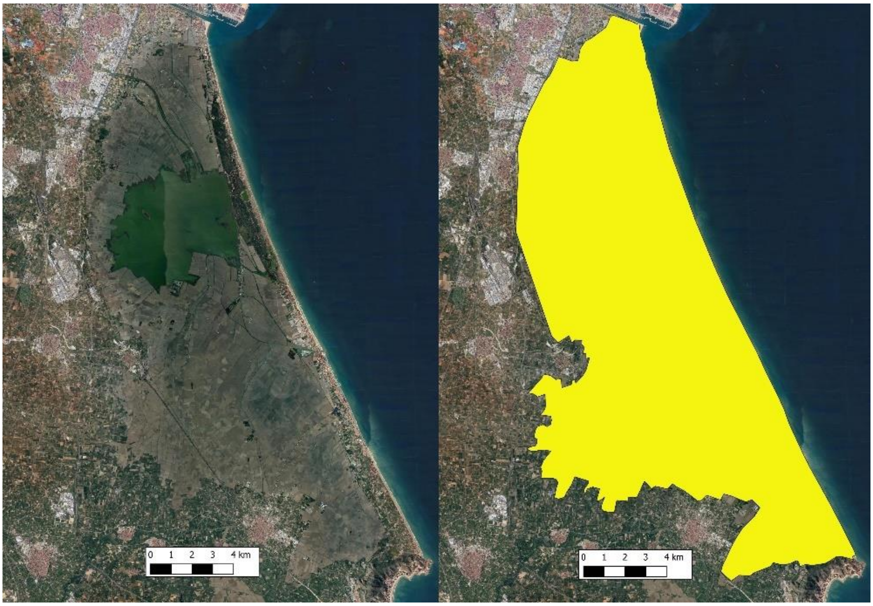

*Fig. 1: Parque Natural de L´Albufera de València, España.*

El Parque Natural de L´Albufera presenta desde hace décadas problemas de contaminación del agua, debido a los vertidos que genera la actividad humana próxima a este espacio natural (Martín *et al*., 2013). Estos problemas se dan en otras zonas de España como puede ser en el Mar Menor en Murcia (García-Pintado *et al*., 2007) o en otros humedales de diferentes países (Ortiz-Reyes and Anex, 2018; Valiela *et al*., 2016).

Además, esta tesis pretende aportar una solución a otro de los grandes problemas medioambientales que se da en las ciudades hoy en día, y que es la mala calidad del aire (Jacobs *et al*., 1997), que se ve perjudicada por la quema de residuos agrícolas como la paja de cereales, como es el caso del arroz (*Oryza sativa*), y otros restos vegetales procedentes de la limpieza y retirada de otras especies invasoras, como es el caso del carrizo (*Phragmites australis*).

Para regular estas quemas y su gestión L´Albufera de València dispone de diferentes figuras de protección, las cuales se deben de tener en cuenta para poder gestionar los residuos vegetales que en el Parque Natural se producen.

1. L´Albufera de València fue declarada Parque Natural el día 8 de julio de 1986 por la Generalitat Valenciana.

2. L´Albufera de València fue incorporada a la Lista de Zonas Húmedas de Importancia Internacional, en la Conferencia Ramsar del 8 de mayo 1990.

3. En 1992 el Parque Natural fue declarado Zona LIC (Lugar de Interés Comunitario) mediante la Directiva 92/43/CEE del Consejo, de 21 de mayo de 1992, relativa a la conservación de los hábitats naturales y de la fauna y flora silvestres.

4. En 1994 fue declarada Área ZEPA (Zona de Especial Protección para Aves) mediante la Directiva 94/24/CE, de 8 de junio de 1994, relativa a la Conservación de las Aves Silvestres.

Así mismo El parque Natural consta de normativa para su gestión:

1. Se establece el régimen jurídico del Parque Natural de L´Albufera de València mediante el Decreto 71/1993, DE 31 de mayo, del Gobierno Valenciano y posteriormente mediante el Decreto 258/2004, de 19 de noviembre, del

Consell de la Generalitat, por el que se modifica el Decreto 71/1993, de 31 de mayo, del Consell de la Generalitat, de Régimen Jurídico del Parque de L'Albufera.

2. En 1995 se aprueba el Plan de Ordenación de los Recursos Naturales (PORN) y mediante el Decreto 96/1995, de 16 de mayo, del Gobierno Valenciano, aprueba el Plan de Ordenación de los Recursos Naturales de la cuenca hidrográfica de L'Albufera. EL PORN viene determinado por el artículo 15.2. de la Ley 4/1989, y de acuerdo con el Decreto 71/1993 de 31 de mayo, de Régimen Jurídico del Parque Natural de la Albufera.

3. En el año 2004 se aprueba el Plan Rector de Uso y Gestión (PRUG) del Parque Natural de L'Albufera mediante el Decreto 259/2004, de 19 de noviembre, del Consell de la Generalitat. Mediante esta normativa se considera el Parque Natural como un recurso prioritario para la Comunidad Valenciana por su interés ecológico, científico y educativo, y también por sus potencialidades en relación con el desarrollo sostenible en materia económica, social y cultural.

También el Parque Natural se ve afectado en cuanto a las quemas por la normativa vigente, ya que está prohibido realizar cualquier tipo de quema, por ello la Conselleria de Agricultura, Desarrollo Rural, Emergencia Climática y Transición Ecológica emite anualmente una resolución de autorización de excepción de quema de rastrojos, regulando las fechas, zonas y formas de quemas en el Parque Natural, siendo la última resolución la Resolución de 14 de octubre de 2019 de autorización de excepción de quema de rastrojos del arroz, campaña 2019, en el Parque Natural de La Albufera (Sollana, València, Cullera, Albalat de la Ribera, Polinyà de Xúquer, Alfafar, Algemesí).

Así mismo mediante el Decreto 259/2004, de 19 de noviembre, del Consell de la Generalitat, por el que se aprueba el Plan Rector de Uso y Gestión del Parque Natural de L'Albufera se prohíbe cualquier tipo de desbroce exceptuando (art. 48 punto 3) el desbroce y monda de las formaciones vegetales propias del margen de las acequias, canales, arrozales y caminos.

Por otro lado, en la investigación también se ha tenido en cuenta la motivación de poder revalorizar los residuos agrícolas y los restos de podas y limpiezas de vegetación adventicia o invasora, cumpliendo así con los objetivos de economía circular de la Unión Europea (Gislev *et al*., 2018). Por ello, también se han incluido en el estudio los residuos de ceniza producidos en una central de biomasa alimentada con paja de cebada (*Hordeum vulgare*), paja de trigo (*Triticum spp.*) y madera de paulownia (*Paulownia spp.*) procedente de cultivos energéticos de crecimiento rápido.

En la bibliografía se pueden encontrar el poder calorífico y el porcentaje de ceniza sobre la biomasa de los materiales estudiados. Así, Jenkins y Ebeling (1985) establecieron el poder calorífico de la paja de arroz, de la paja de trigo y de la paja de cebada, siendo 16,28 $MJ\cdot Kg^{-1}$, 17,51 $MJ\cdot Kg^{-1}$ y 17,31$MJ\cdot Kg^{-1}$ respectivamente. Además, establecieron el porcentaje de ceniza sobre biomasa de la paja de arroz, de la paja de trigo y de la paja de cebada, siendo 13,24%, 8,24% y 10,29% respectivamente. Kitzler *et al*. (2012) establecieron el poder calorífico del carrizo 16,187 $MJ\cdot Kg^{-1}$ y el porcentaje de ceniza sobre biomasa en el 7,47%. Por último, López *et al*. (2012) establecieron el poder calorífico de la *Paulownia robusta* en 20,3 $MJ\cdot Kg^{-1}$ y el porcentaje de ceniza sobre biomasa en el 0,89%.

## 1.2 Estado del arte

En este apartado se analizan las aportaciones científicas más recientes y relevantes en relación con depuración de aguas residuales mediante procesos de adsorción. Para ello, se ha realizado una revisión bibliográfica de artículos publicados en los últimos años en relación con la temática de la tesis

Los artículos para realizar el estudio bibliográfico han sido buscados en la web (https://www.recursoscientificos.fecyt.es/), que es la base de datos WOS (Web of Science).

Los términos buscados han sido: "adsorption" and "wastewater", "adsorption" and "phosphorus", "adsorption" and "ash", "adsorption" and "Eutrophication" y "adsorption" and "agro-waste" para un periodo de tiempo de 30 años (1990-2019).

Para elaborar la figura 2 se ha calculado un acumulado del número de artículos publicados por año para cada una de las categorías introducidas en las búsquedas. A partir de los datos acumulados se ha realizado una gráfica logarítmica para poder percibir con mayor resolución la evolución de las búsquedas a lo largo del tiempo.

En la Figura 2 se puede observar que en las últimas tres décadas ha habido un importante incremento de la producción científica con relación a la temática estudiada. Se puede observar en la bibliografía consultada que los procesos de adsorción suelen estar ligados a aguas residuales, a fósforo, a cenizas y a eutrofización. También cabe destacar que desde 2006 se comienzan a estudiar los procesos de adsorción con residuos agrícolas.

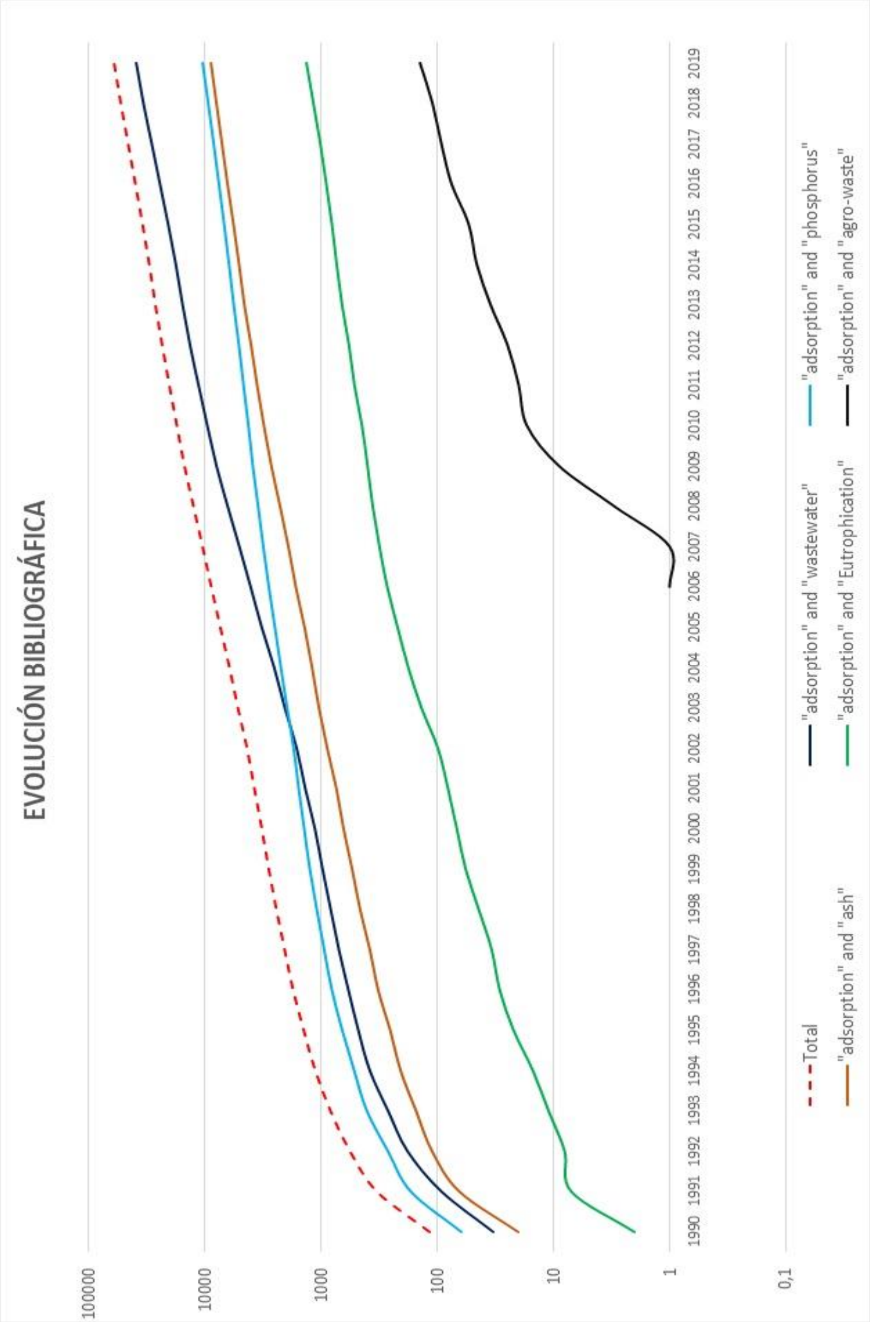

*Fig. 2: Gráfica de la evolución bibliográfica.*

Además de estudiar la producción científica relacionada con la temática de la tesis, se han revisado los principales artículos publicados durante los últimos años para conocer en detalle el estado del arte. Aquí se detallan los principales resultados y conclusiones de los más relevantes y citados a nivel mundial.

**Cita**: (Yadav *et al*., 2015)

**Adsorbente**: Residuo de zumo de fruta y cáscara de arroz triturado.

**Adsorbato**: Fosfato.

**Objetivo**: El objetivo del presente estudio es investigar el posible uso de residuos de empresas productoras de zumo de fruta (*Citrus limetta*) y cáscara de arroz como adsorbentes para la eliminación de fosfato de disoluciones acuosas.

**Conclusiones**: La muestra que el residuo de zumo de fruta puede considerarse como un adsorbente eficiente para el tratamiento de aguas residuales ricas en fosfato.

**Cita**: (Mor *et al*., 2016)

**Adsorbente**: Ceniza de cáscara de arroz

**Adsorbato**: Fosfato.

**Objetivo**: El objetivo de este artículo es el estudio de la capacidad de adsorción del fosfato mediante el residuo de una planta de biomasa.

**Conclusiones**: Este estudio concluye que la cáscara de arroz activada con HCl es un adsorbente eficiente y rentable del fosfato de las aguas residuales.

**Cita**: (Wang *et al*., 2017)

**Adsorbente**: Zeolita modificada con Lantano, que se obtuvo a partir de cenizas de carbón.

**Adsorbato**: Fosfato.

Objetivo: El objetivo de este estudio es conocer la capacidad de reducción de la concentración de fosfato disuelto en lagos mediante la adsorción de este fosfato con Zeolitas obtenidas a partir de cenizas de carbón modificadas con Lantano.

**Conclusiones**: La zeolita obtenida a partir de cenizas de carbón modificada con Lantano es capaz de adsorber el fósforo del agua, con lo cual este material sería apto para controlar la cantidad de fósforo del agua en lagos.

**Cita**: (Sima *et al*., 2018)

**Adsorbente**: Ceniza de clincke y residuo de óxido de hierro.

**Adsorbato**: Fósforo.

**Objetivo**: El objetivo de este artículo es comparar las capacidades de adsorción del fósforo de los relaves de óxido de hierro y los residuos de cenizas de clincke de la minería de cobre y níquel en Botsuana.

**Conclusiones**: El estudio concluye que el óxido de hierro tiene una mayor capacidad de adsorción de fósforo que las cenizas de clincke.

**Cita**: (Zhou *et al*., 2019).

**Adsorbente**: Pellets de ceniza y carbón.

**Adsorbato**: Fósforo.

**Objetivo**: El objetivo de este estudio es evaluar la capacidad de adsorción de carbón y cenizas como adsorbentes granulados para la reutilización del fósforo disuelto en agua.

**Conclusiones**: Este estudio concluye que se pueden utilizar las cenizas perladas para la adsorción del fósforo.

**Cita**: (Tovar-Gómez *et al*., 2015)

**Adsorbente**: Carbón activo con desechos de huevo.

**Adsorbato:** Multicomponente de tinte azul ácido 25 (AB25) e iones de metales pesados (Zinc, Níquel y Cadmio).

**Objetivo**: El objetivo de este estudio es conocer la capacidad de adsorción del tinte azul ácido 25 (AB25) y de los iones de metales pesados (Zinc, Níquel y Cadmio) mediante carbón activo con desechos de huevo.

**Conclusiones**: La conclusión del estudio es que la eliminación de componentes múltiples de zinc, níquel, cadmio y colorante AB25 en carbón activado puede mostrar adsorción tanto sinérgica como antagonista.

**Cita**: (Paradelo *et al*., 2016)

**Adsorbente**: Cascara de mejillón.

**Adsorbato**: Fósforo.

**Objetivo**: El objetivo de este estudio es estudiar la capacidad de adsorción de fósforo en procesos discontinuos y continuos mediante cascara de mejillón.

**Conclusiones**: La conclusión a la cual se ha llegado es que la cascara de mejillón ayuda a la eliminación de fósforo de dos métodos, mediante adsorción y mediante precipitación.

**Cita**: (Hermassi *et al*., 2017)

**Adsorbente**: Cenizas de centrales eléctricas de carbón.

**Adsorbato:** Fósforo.

**Objetivo**: El objetivo de este estudio es evaluar la viabilidad de la eliminación y recuperación del fósforo mediante la adsorción con cenizas generadas en las centrales eléctricas de carbón.

**Conclusiones**: Este estudio llega a la conclusión de que la ceniza de centrales eléctricas es un buen adsorbente de fósforo y que además sirve como fertilizante una vez finalizada su vida útil.

**Cita**: (Delgadillo-Velasco *et al*., 2018)

**Adsorbente**: Carbonos activados, compuesto de carbón óseo, sílice natural, zeolita natural, compuesto de óxido de manganeso (II) e hidróxido de hierro (III).

**Adsorbato:** Fosfato.

**Objetivo**: El objetivo de este estudio es conocer la capacidad de adsorción de diferentes adsorbentes y evaluar cuál es el que posee mayor capacidad de adsorción.

**Conclusiones**: La conclusión del estudio es que la adsorción de fosfatos sigue el siguiente orden de mayor a menor capacidad de adsorción: hidróxido de hierro (III) compuesto de óxido de manganeso (II), compuesto de carbón óseo activo, carbonos activados, sílice y zeolita naturales. Además, se concluye que el hidróxido de hierro (III) es muy selectivo en cuanto al fosfato tanto para aguas residuales reales como para las aguas sintéticas.

**Cita**: (López *et al*., 2019)

**Adsorbente**: Residuo de hidrato de silicato de calcio.

**Adsorbato:** Fosfato.

**Objetivo**: El objetivo de este estudio es conocer la capacidad de adsorción del fosfato procedente del tratamiento de aguas residuales mediante el residuo de hidrato de silicato de calcio en proceso discontinuo.

**Conclusiones**: Se concluye que la retención de fosfato se produce principalmente por procesos de adsorción y una pequeña fracción queda retenida por precipitación. También se determina qué material cargado de fosfato se puede emplear para la mejora de suelos agrícolas deficientes en fósforo.

## 1.3 Justificación de la investigación

La investigación recogida en esta tesis se justifica por diversas razones, siendo la principal la necesidad de ampliar el conocimiento en las técnicas o metodologías que mejoren la calidad de las diferentes masas de agua con un bajo coste (Bhatnagar and Sillanpää, 2010; Mohan *et al*., 2014; Trivedy and Kaul, 1996), ya que en este campo científico no hay metodologías que sean claramente más beneficiosas que otras para todos los lugares del mundo (Bhatnagar and Sillanpää, 2010; Mohan *et al*., 2014; Trivedy and Kaul, 1996).

Estas técnicas pueden contribuir a reducir sustancialmente la cantidad de elementos químicos disueltos en el agua, como es el caso del fósforo, principal causante junto con el nitrógeno de la eutrofización, que es uno de los mayores problemas que presenta el lago de L'Albufera de València (Schindler *et al*., 2008).

Otro aspecto de interés de esta investigación es la utilización y revalorización de residuos vegetales como adsorbentes. El tipo de residuos y sus posibles mezclas serán diferentes para cada lugar del mundo puesto que el tipo de biomasa disponible será distinto.

Por otra parte, la gestión de la biomasa residual consistente en su quema controlada al aire libre agrava uno de los problemas medioambientales más comunes en las ciudades, que es la contaminación del aire (Jacobs *et al*., 1997). En la zona de estudio la principal biomasa quemada es la paja de arroz y los restos de la limpieza y eliminación del carrizo como especie invasora. Una adecuada gestión de estos residuos eliminaría la contaminación producida y que afecta a la ciudad de València y otros municipios próximos.

Por todos estos motivos, y como se puede observar en la figura 2, la cantidad de aportaciones científicas en esta temática va aumentando de forma exponencial, ya que los procesos de adsorción representan una de las mejores alternativas para la depuración de aguas residuales al menor coste posible (Siyal *et al*., 2020; Trivedy and Kaul, 1996).

De hecho, el estudio de los procesos de adsorción con agro-residuos o residuos vegetales en general es un campo de investigación que está en aumento desde el año 2006, debido a la caracterización y mejor conocimiento de las propiedades de los materiales adsorbentes, en especial su capacidad de adsorción (Miretzky and Cirelli, 2010).

# 2. OBJETIVOS

## 2.1 Objetivo general

El objetivo general de la investigación desarrollada es analizar y evaluar la posibilidad de utilizar residuos vegetales para la eliminación de fósforo en aguas residuales mediante procesos de adsorción.

## 2.2 Objetivos específicos

Para alcanzar el objetivo general, la investigación cuenta con tres objetivos específicos (OE), correspondiendo cada uno de ellos con los capítulos en los que se estructura la tesis.

OE1. El primer objetivo específico consiste en analizar la alternativa al uso de ceniza de paja de arroz como fertilizante natural reduciendo la contaminación de fósforo en humedales protegidos.

OE2. El segundo objetivo específico es analizar la posibilidad de uso de ceniza de *Phragmites australis* para el control de la contaminación de fósforo en ecosistemas de humedales antropogénicos.

OE3. El tercer objetivo específico de la tesis es analizar y cuantificar la reducción del fósforo de aguas residuales a través de procesos de adsorción reutilizando ceniza de madera y paja generada en instalaciones bioenergéticas.

## 2.3 Objetivos operativos

Los tres objetivos específicos se alcanzan por los objetivos operativos (OO) de la investigación, que se estructuran en los tres capítulos de la tesis.

Los objetivos operativos dentro del Capítulo I (*Alternativa al uso de paja de arroz como fertilizante natural reduciendo la contaminación de fósforo en humedales protegidos*), son:

OOI1. Caracterizar los materiales de ceniza de paja de arroz, tanto tratada con HCl (1M) como sin tratar.

OOI2. Determinar las cinéticas de adsorción de la ceniza de paja de arroz, tanto tratada con HCl (1M) como sin tratar, para la eliminación de fósforo.

OOI3. Determinar las isotermas de adsorción de Langmuir, Tempkin y Freundlich del fósforo para las temperaturas de 283, 293 y 303 K.

OOI4. Determinar los efectos de la temperatura sobre las capacidades de adsorción máximas ($q_{max}$).

OOI5. Determinar los efectos de la dosis de adsorbente sobre la capacidad de adsorción de fósforo.

OOI6. Determinar los efectos de la dosis de adsorbente sobre las capacidades de adsorción máximas ($q_{max}$).

OOI7. Determinar los efectos de la carga iónica y de los cationes de calcio sobre la capacidad de adsorción de fósforo.

OOI8. Determinar el efecto tampón de pH de las cenizas de paja de arroz, tanto tratada con HCl (1M) como sin tratar.

OOI9. Determinar las entalpias de adsorción de la ceniza de paja de arroz, tanto tratada con HCl (1M) como sin tratar.

Los objetivos operativos dentro del Capítulo II (*Uso del Phragmites australis para el control de la contaminación de fósforo en ecosistemas de humedales antropogénicos*), son:

OOII1. Caracterizar la ceniza de carrizo (*Phragmites australis)*.

OOII2. Determinar las cinéticas de adsorción de la ceniza de carrizo para la eliminación de fósforo.

OOII3. Determinar las isotermas de adsorción de Langmuir, Tempkin y Freundlich del fósforo para las temperaturas de 283, 293 y 303 K.

OOII4. Determinar los efectos de la temperatura sobre las capacidades de adsorción máxima ($q_{max}$).

OOII5. Determinar los efectos de la dosis de adsorbente sobre la capacidad de adsorción de fósforo.

OOII6. Determinar los efectos de la dosis de adsorbente para la máxima capacidad de adsorción ($q_{max}$).

OOII7. Determinar los efectos de la carga iónica y de los cationes de calcio sobre la capacidad de adsorción de fósforo.

OOII8. Determinar el efecto tampón de pH de la ceniza de carrizo en la disolución.

OOII9. Determinar las entalpias de adsorción de la ceniza de carrizo.

OOII10. Determinar la capacidad de adsorción de mezclas de ceniza de paja de arroz y de ceniza de carrizo.

Los objetivos operativos dentro del Capítulo III (*Reducción de fósforo de aguas residuales a través de procesos de adsorción reutilizando ceniza de madera y paja producida en instalaciones bioenergéticas*), son:

OOIII1. Caracterizar las cenizas de madera de paulonia, paja de trigo y paja de cebada.

OOIII2. Determinar las cinéticas de adsorción de las cenizas de madera de paulonia, paja de trigo y paja de cebada para la eliminación de fósforo.

OOIII3. Determinar los efectos de la dosis de adsorbente sobre la capacidad de adsorción de fósforo.

OOIII4. Determinar los efectos de la dosis de adsorbente para las máximas capacidades de adsorción ($q_{max}$).

OOIII5. Determinar las isotermas de adsorción de Langmuir, Tempkin y Freundlich del fósforo para las temperaturas de 283, 293 y 303 K.

OOIII6. Determinar los efectos de la temperatura para las máximas capacidades de adsorción ($q_{max}$).

OOIII7. Determinar las entalpias de adsorción de las cenizas de madera de paulonia, paja de trigo y paja de cebada.

# 3. ESTRUCTURA DE LA TESIS

El presente documento está formado por diez secciones.

- La primera sección está compuesta por una introducción general, donde se indica que ha motivado la investigación, se desarrolla una revisión del estado del arte de la temática tratada y se justifica la investigación.

- En la segunda sección se enumeran el objetivo general de la investigación, los objetivos específicos que se han establecido para poder conformar el objetivo general y, por último, los objetivos operativos. Estos últimos son los objetivos instrumentales de la investigación que se han plantean para poder alcanzar cada objetivo específico, y son la base de los experimentos en campo y en laboratorio.

- La tercera sección de esta tesis está dedicada a explicar la estructura de la tesis y con ello ayudar a su comprensión.

- La cuarta, quinta y sexta secciones están dedicadas a los tres objetivos específicos de la investigación. Cada sección corresponde con un artículo, los cuales tienen la típica estructura de aportación científica, constando de: Introducción, objetivos, materiales y métodos, resultados y discusión y conclusiones.

- La séptima sección comprende las conclusiones generales de toda la investigación y formula futuras líneas de investigación basadas en el conocimiento científico adquirido en la presente investigación.

- La octava sección describe la transferencia de los resultados de la investigación y se citan y explican las publicaciones científicas, la participación en congresos, conferencias y seminarios.

- La novena sección lista y detalla las referencias bibliográficas de todo el documento.

- Por último, se incluye la décima sección con los documentos anexos de los Capítulos I, II y III.

# 4. CAPITULO I: ALTERNATIVA AL USO DE PAJA DE ARROZ COMO FERTILIZANTE NATURAL REDUCIENDO LA CONTAMINACIÓN DE FÓSFORO EN HUMEDALES PROTEGIDOS. *ALTERNATIVE USE OF RICE STRAW ASH (Oryza sativa) AS NATURAL FERTILIZER TO REDUCE PHOSPHORUS POLLUTION IN PROTECTED WETLAND ECOSYSTEMS.*

# CAPITULO I

**Referencia de la publicación:**

Carricondo, J.M., González, J.A., Mengual, J., Turégano, J.V., Oliver-Villanueva, J.V., (2020). Alternative use of rice straw ash as natural fertilizer to reduce phosphorus pollution in protected wetland ecosystems. *International Journal Recycling of Organic waste in Agriculture*. 9:61-74. https://doi.org/10.30486/IJROWA.2020.1885299.1003

# 4. CAPITULO I: ALTERNATIVA AL USO DE PAJA DE ARROZ COMO FERTILIZANTE NATURAL REDUCIENDO LA CONTAMINACIÓN DE FÓSFORO EN HUMEDALES PROTEGIDOS. *ALTERNATIVE USE OF RICE STRAW ASH (Oryza sativa) AS NATURAL FERTILIZER TO REDUCE PHOSPHORUS POLLUTION IN PROTECTED WETLAND ECOSYSTEMS.*

## 4.1. 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 S., Crosetti D., 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).

The Natural Park L'Albufera de València 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 determinated 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 Fernández *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.

## 4.2. Materials and methods

### 4.2.1. 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 S., Crosetti D., 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 València 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 to 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.

### 4.2.2. 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 $HNO_3$/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 Kα 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 $N_2$ 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 pHPZC, 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.

### 4.2.3. Batch adsorption experiments

Adsorption experiments were carried out in batch mode by using different concentration (5-100 mgP $L^{-1}$) of sodium phosphate dibasic ($Na_2HPO_4$) 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 dose varying from 5-24 g $L^{-1}$. After finishing adsorption experiment, the solution was filtered through glass microfiber filter (1.2 µm). 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.

### 4.2.4. 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:

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

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:

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

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:

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

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.

## 4.3. Results and discussion

### 4.3.1. 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. 3 and ANEXO 1) 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 |

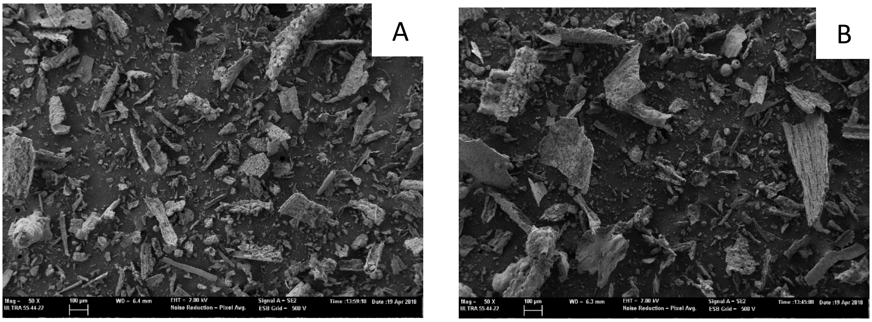

*Fig. 3: Scanning electron micrograph of adsorbents: A) RSA and B) RSA-H.*

Diffraction pattern of the different ashes (Figure. 4) 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. Figure 5 shows the plot used to determine the pH at point of zero charge of both adsorbents (see also table 1).

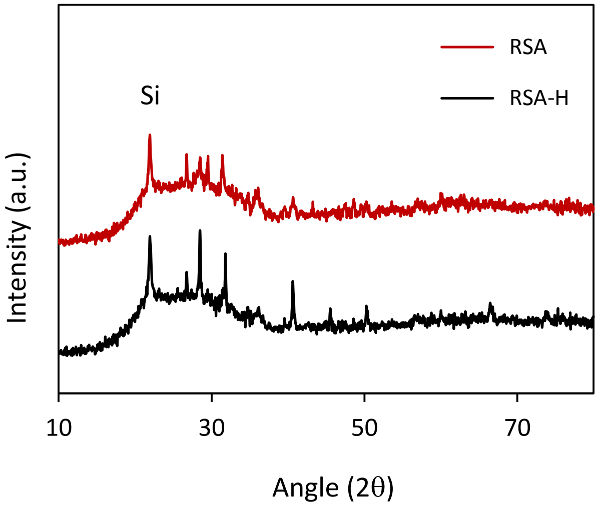

*Fig. 4: X-ray diffraction of adsorbents.*

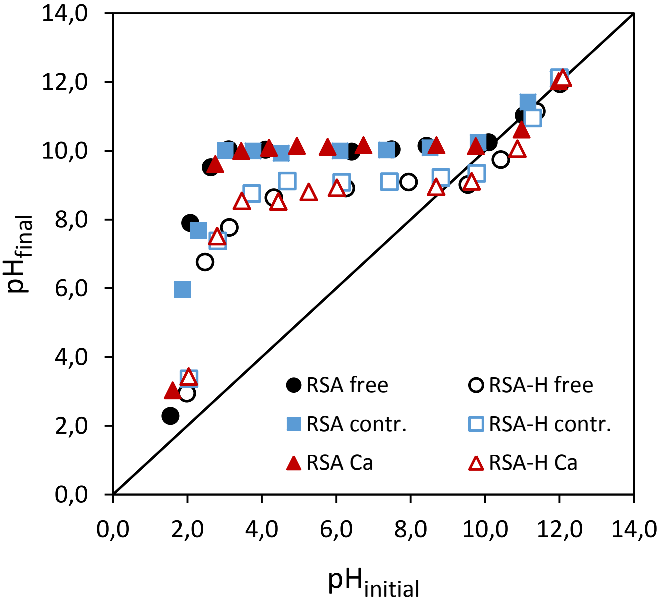

*Fig. 5: Determination of the point of zero charge for both adsorbents.*

The basicity of the samples can be observed (Figure 5) 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 $CaCl_2 \cdot 4H_2O$ solution in adsorbent Ca captions, did not produce any appreciable effect in neither of the two adsorbents.

### 4.3.2. 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. 6.

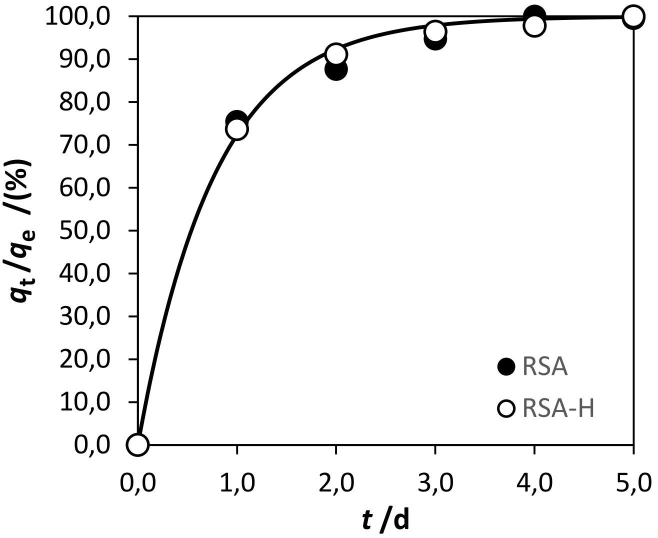

*Fig. 6: Kinetics of phosphate removal by both adsorbents at 283 K. Dose of adsorbent, 10 g $L^{-1}$. Initial phosphate concentration, 60 mgP $L^{-1}$.*

Taking it into account, phosphate adsorption isotherms at three different temperatures of RSA (Figure 7) and RSA-H (Figure 8) 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) and 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 $R^2$.*

| | | RSA | | | RSA-H | | |
|---|---|---|---|---|---|---|---|
| Models | T /K | 283 | 293 | 303 | 283 | 293 | 303 |
| Langmuir | $q_{max}$/(mg $g^{-1}$) | 3.39 | 4.45 | 5.24 | 2.23 | 2.82 | 3.22 |
| | $K_L$/(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 |
| | DAIC | 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 |
| | DAIC | 95.3 | | | | | |
| Tempkin | $B$ (mg $g^{-1}$) | 0.726 | 0.907 | 1.04 | 0.503 | 0.623 | 0.700 |
| | $K_T$ (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 |
| | DAIC | 4.8 | | | | | |

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

Table 2 shows the fitted parameters of the three studied isotherm models, including coefficients of determination ($R^2$). To avoid getting meaningless parameters, all the models have been fitted directly, without any transformation to create a linear graph (Fig. 37 and ANEXO 1), 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.

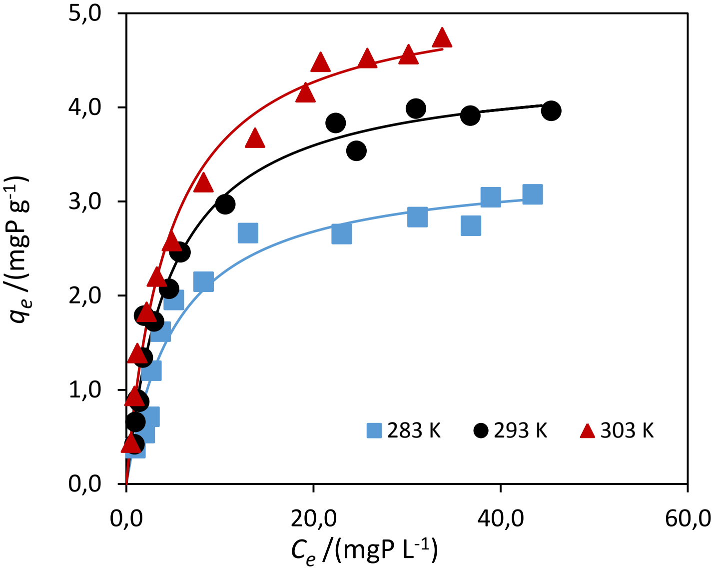

*Fig. 7: Phosphate adsorption isotherms at different temperatures for RSA.*

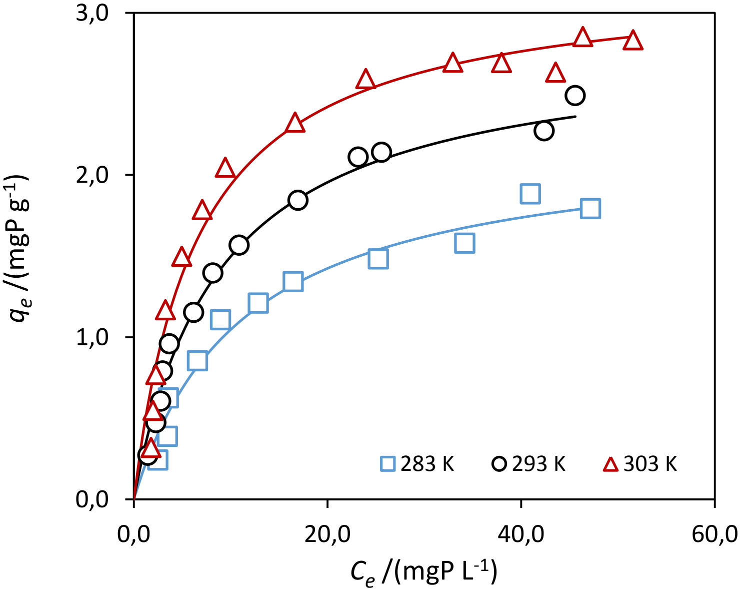

*Fig. 8: Phosphate adsorption isotherms at different temperatures for RSA-H.*

Figure 7 shows the fitted curves obtained for the Langmuir model for RSA and Figure 8 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 figure 9. This variation is lineal and shows a significantly higher growth rate, almost double, in RSA than in RSA-H adsorbent.

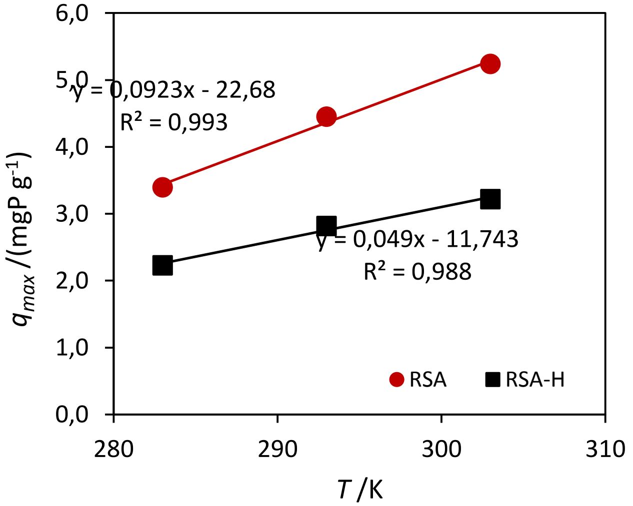

*Fig. 9: Effect of temperature on maximum capacity of adsorption.*

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 (${}_{ad}H$º) using the van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial (1/T)}\right)_{\theta} = -\frac{\Delta_{ad}H^{\circ}}{R} \qquad (4)$$

Figure 10 shows the graphical representation of the van't Hoff equation of the experimental data. 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.

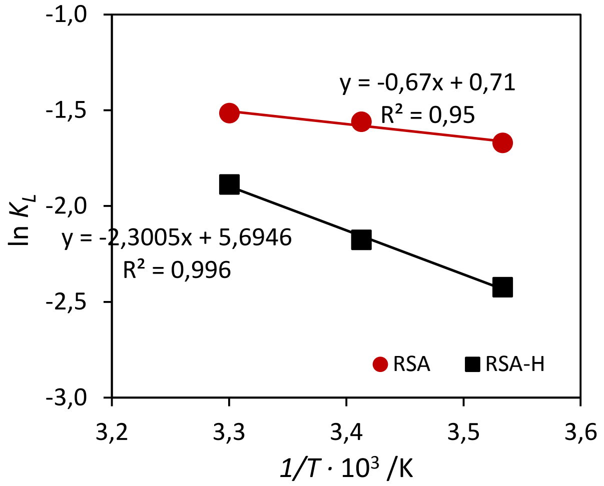

*Fig. 10: Effect of temperature on the Langmuir constant.*

### 4.3.3. Effect of adsorbent dose

Once again, Langmuir model shows the best results. Figure 11 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, figure 11 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.

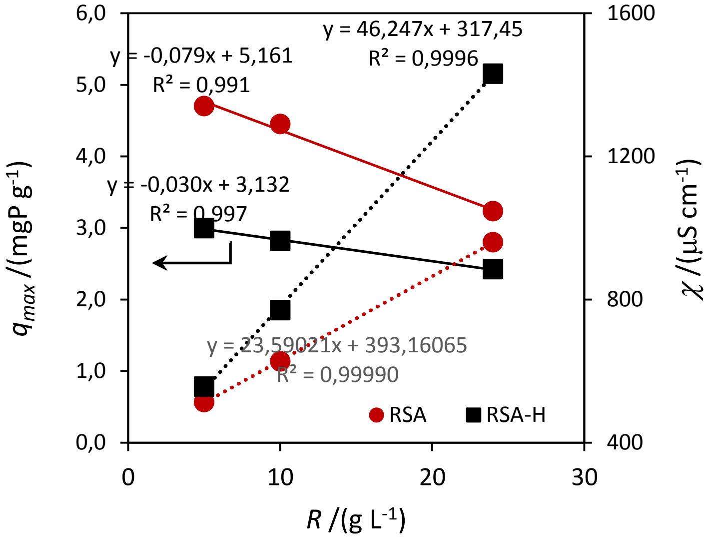

*Fig. 11: Effect of adsorbent dose in the maximum capacity of adsorption at 293 K for both adsorbents.*

### 4.3.4. 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 figure 11. 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.

Figure 12 shows the effect of ionic strength in the adsorption for RSA adsorbent and Figure 13 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 (10-80 mgP $L^{-1}$). The figures allow comparing the behaviour of the original sample (average conductivity around 630 mS $cm^{-1}$ and 770 mS $cm^{-1}$ 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 (figure 12), 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.

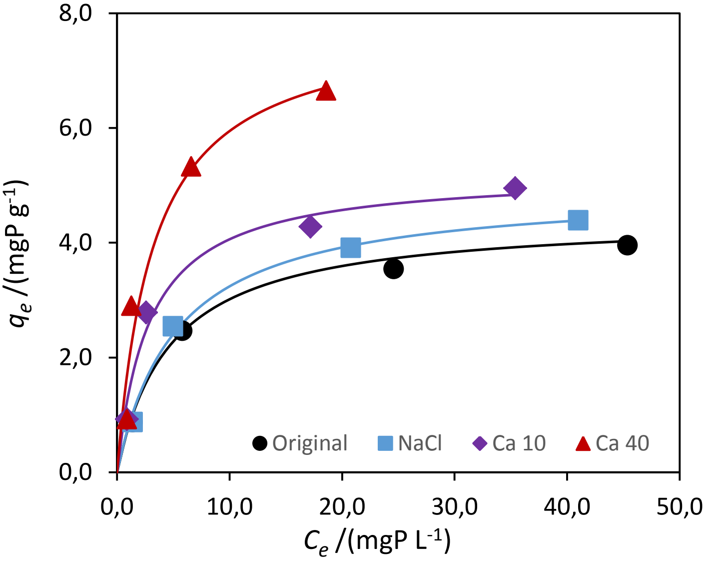

*Fig. 12: Effect of ionic strength and calcium in the phosphate removal at 293 K for RSA.*

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 $CaCl_2·4H_2O$. The tests were done with a controlled ionic strength around 2.50 mS $cm^{-1}$ 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. Figure 13 shows the results for RSA-H material.

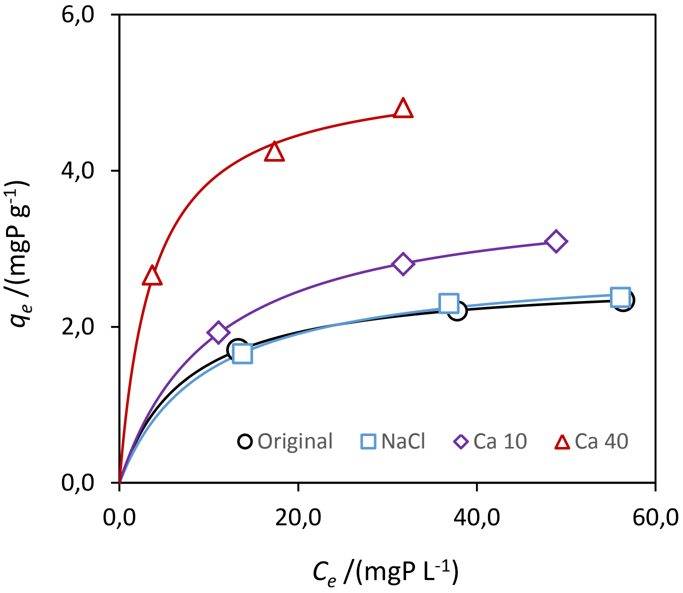

*Fig. 13: Effect of ionic strength and calcium in the phosphate removal at 293 K for RSA-H.*

## 4.4. 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.

# 5. CAPITULO II: USO DEL CARRIZO (*Phragmatites australis*) PARA EL CONTROL DE LA CONTAMINACIÓN DE FÓSFORO EN ECOSISTEMAS DE HUMEDALES ANTROPOGÉNICOS. USE OF COMMON REED (*Phragmites australis*) FOR CONTROLLING PHOSPHORUS CONTAMINATION IN ANTHROPOGENIC WETLAND ECOSYSTEMS.

# CAPITULO II

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## 5.1. Introduction

Common reed (*Phragmites australis* (Cav.) Trin. ex Steud.) is an invasive species that commonly forms extensive stands of reed beds around water lagoons and rivers. Common reed is very important for wildlife and conservation, particularly in Europe and Asia, where several species of migratory birds are strongly tied to large reed stands (Fasola and Ruiz, 1996; Rodrigo *et al*., 2018). On the other hand, in North America P. australis is commonly considered an exotic and often-invasive species, introduced from Europe (Saltonstall, 2002). Moreover, reed has several traditional and cultural uses in agriculture (e.g. baskets) and housing (e.g. thatching roofs) (Hulshof and Vos, 2016).

Reed is one of the main wetland plant species used for phytoremediation water treatment (Ahmad *et al*., 2014). So, some authors (Chandra and Yadav, 2011) demonstrated that these wetland plants could be used for heavy metal phytoremediation of contaminated agricultural, domestic or even industrial wastewater. Reed has also been used in constructed wetlands, i.e. engineered systems that use the natural functions of vegetation, soil and organisms to treat agricultural, municipal or industrial wastewater, greywater or stormwater runoff (Hoffmann *et al.*, 2011). Similarly to natural wetlands, constructed wetlands also act as biofilters and/or can remove a range of pollutants (such as organic matter, nutrients, pathogens, heavy metals) from the water (Brix *et al.*, 2007).

Research work shows that increasing nitrogen and phosphorus concentration increases eutrophication in wetlands (Del Barrio Fernández *et al.*, 2012; Vybernaite-Lubiene *et al.*, 2017). Furthermore, other authors (Uddin and Robinson, 2018) report that by increasing nitrogen and phosphorus concentrations in wetland waters, invasive plants, such as P. australis grow faster and form dense thickets of vegetation. So, reed displaces autochthonous plant species, such as wild rice, cattails and native wetland orchids (Ailstock *et al.*, 2001; Coleman and Levine, 2007). Reed has a high above-ground biomass that blocks out light to other plants (Farnsworth and Meyerson, 2003), allowing areas to turn into monoculture very quickly (Holdredge and Bertness, 2011). Anthropogenic wetlands combine natural vegetation with agricultural crops, especially rice plantations (Setter *et al.*, 1995; Verhoeven and Setter, 2010). Research work (Pinto *et al.*, 2016) analysed essential and nonessential/toxic elements in 86 rice types produced in wetlands all around the world. The obtained average content of the essential elements are 1189 mg $kg^{-1}$ (P), 746 mg $kg^{-1}$ (K), 294 mg $kg^{-1}$ (Mg), 84.7 mg $kg^{-1}$ (Ca), 13.3 mg $kg^{-1}$ (Zn), 8.8 mg $kg^{-1}$ (Na), 8.3 mg $kg^{-1}$ (Mn), 7.5 mg $kg^{-1}$ (Fe), 1.9 mg $kg^{-1}$ (Cu), 0.55 mg $kg^{-1}$ (Mo), 0.18 mg $kg^{-1}$ (Se) and 0.12 mg $kg^{-1}$ (Co). These elements are present in the rice fields, so that the plants can feed on them; NPK being the most necessary nutrients (Singh and Singh, 2017). Phosphorus inputs are produced in these wetlands due to agricultural fertilizers and wastewater discharges that do not have phosphorus elimination or filtering systems (Correll, 1998; Li *et al*., 2016; Maiga *et al*., 2017; N. Sharpley *et al*., 1994).

Furthermore, other studies show how the reed growth influences directly the concentration decrease of macronutrients such as phosphorus (Uddin and Robinson, 2018) as well as heavy metals (Hernández-Crespo and Martín, 2015; Vymazal and Březinová, 2016). Therefore, pruning reed in wetlands can be considered a good environmental practice since macronutrients such as N and P are extracted from the water, taking into account that a high concentration of these elements generates eutrophication (Zhang *et al*., 2018).

The decrease of chemical elements concentrated in water by the absorption of reed does not occur equally over the life of the plant (Rai, 2008). So, the growing regime determines the absorption of the nutrients. There is a linear relationship between reed biomass growth and N and P abstraction (Meuleman *et al*., 2002). This annual growth depends on the type of wetland, from 32 t $ha^{-1}$ $year^{-1}$ in natural wetlands to 70 t $ha^{-1}$ $year^{-1}$ in infiltration wetlands (Meuleman *et al*., 2002).

The best harvesting time of reed biomass is determined by the flowering. Reed has to be pruned before the seeds are released at the moment of maximum biomass and higher nutrients concentration (N and P). So, the parts of the plants in senescence neither detach from the plant nor return the nutrients to the water, avoiding problems of eutrophication (Meuleman *et al*., 2002).

The pruning process of reed in the wetlands generates residual biomass that can be used for bioenergy generation in biomass plants (Matsumura *et al*., 2005; Važić *et al*., 2015).Reed ash (RA) is generated as waste in the industrial combustion process.

One interesting alternative solution for an effective waste management is to reincorporate this ash into the rice plantations, with the principal aim of removing phosphorus, but also taking advantage of the capacity of reed to adsorb heavy metals (Kumari and Tripathi, 2015) existing in wetland lagoons like Zn, Cu, Ni and Pb (Boluda *et al*., 1993). This opportunity for waste valorization is also based on the experiences described by other authors (Ugurlu and Salman, 1998; Yadav *et al*., 2015), who demonstrate the capacity of other plant ashes for the elimination of phosphorus in contaminated waters.

Thus, the main objective of this research is to analyse the feasibility of using common reed (*P. australis*) for controlling phosphorus contamination in anthropogenic wetland ecosystems. To achieve this objective, the research focuses on the use of the RA, generated in bioenergy plants, in the removal of phosphate from contaminated water in the same wetland where the reed is growing. To do this, batch-type experiments were developed to analyse the effect of several parameters on phosphorus removal. These parameters are mainly contact time, phosphorus–ash ratio, ash dose and temperature. Furthermore, the research aims to assess the viability of using ashes from other plant materials produced by wetland agriculture (specifically rice straw ash (RSA)) to complement the obtained RA in order to eliminate phosphorus.

Finally, following the experiences of other authors with other plant ashes (El-Sobky, 2017; Smol *et al*., 2015), the research also analyses the subsequent utilization of RA, after phosphorus removal, as a natural fertilizer in wetland rice plantations, closing the circular economy system (Smol *et al*., 2015).

## 5.2. Materials and methods

### 5.2.1. Preparation of testing material

Reed samples for the experiments were obtained from the L'Albufera wetland located 10 km south of València (Spain). It is a freshwater lagoon and estuary on the Gulf of València coast, in eastern Spain. It represents the main portion of the Valencian L'Albufera Natural Park, with a surface area of 21,120 hectares. The natural biodiversity found here allows for a great variety of flora and fauna all year-round. Though once a saltwater lagoon, dilution due to irrigation and canals draining into the estuary, as well as sand bars increasing in size, had converted it to freshwater by the seventeenth century. Rice growing has been the most important traditional use of this land since the eighteenth century. It has great environmental importance, apart from the economic, because plant and animal species that have disappeared from the lake itself still live in the surrounding rice fields, where the water of the lagoon is purified. These rice paddies also provide food and shelter for many birds. L'Albufera is a complex anthropogenic wetland ecosystem and is included in the Convention on Wetlands of International Importance (RAMSAR list).

The aquatic vegetation occupies 300 hectares around the lagoon. It is formed by submerged, floating and marshy communities, which have great biodiversity and singular importance. This vegetation inhabits flooded areas during a great part of the year, although also permanent waters, with the roots inside the water and the stem and the leaves emerged. The main species is reed (*P. australis*), accompanied by other aquatic species such as *Scirpus lacustris*, *Typha latifolia*, *Cladium mariscus* and *Kosteletzkya pentacarpos*.

The testing material was obtained from the pruning of a mature stand of reed in the area of El Palmar (Geographical coordinates: 39,315676085065256, −0,3197024279343168).

20 kg of reed biomass was harvested and transported to the bioenergy plant located in Ademuz, València, Spain. After the combustion process, 1.518 kg of RA was transported to the lab for the tests.

### 5.2.2. Preparation and characterization of adsorbents

The RA was heated at 778 K for 1 h in a muffle furnace, losing 20–22% of total weight. Thereafter, RA was washed with distilled water until the conductivity was under 1000 µS cm$^{-1}$. Next, RA was dried at 378 K 24 h in an oven to achieve constant weight. Finally, following the recommendations of other authors (Mor *et al.*,

2016) RA was sieved with a 1 mm grid sieve to ensure uniform particle size for the lab tests.

Characterization of adsorbents was done using different techniques. To determine the major and trace elements present in the adsorbent, chemical analyses were carried out in an optical emission spectrometer (Varian 715-ES ICP), after dissolution in $HNO_3$/HCl/HF. Elemental RA analysis (C, H, N, S) was performed on a thermo-organic element analyser Fisons EA 1108 CHNS-O. To know the crystalline nature of the material, powder X-ray diffraction 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 Kα 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.

Additionally, textural properties were determined by $N_2$ adsorption–desorption isotherms measured on a Micromeritics ASAP 2020 at 77 K. The pH and electrical conductivity measurements of RA were carried out on a pH meter and conductometer MULTI 340i. Following other laboratory experiences (Setter *et al.*, 1995), pH and electrical conductivity of RA were measured after stirring distilled water with raw ash with a ratio of 1/10 (V/W) for 10 min.

### 5.2.3. Adsorption isotherms and kinetics

In order to determine the adsorption capacity of RA, adsorption isotherm experiments were conducted varying contact time from 0 to 120 h with an initial phosphorus concentration of 80 ppm at different temperatures (283, 293 and 303 K), following the recommendations of other authors (Ahmaruzzaman, 2010; Seliem *et al.*, 2016). Adsorption isotherms show the relation between the total mass adsorbed per gram of adsorbent, qe (mg $g^{-1}$), and the equilibrium concentration of adsorbate, Ce (mg $L^{-1}$), at constant temperature and pH (Tran, 1997). Three adsorption isotherm models have been applied for the lab experiments: Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Temkin (Temkin, 1941).

The Langmuir adsorption model (Langmuir, 1916) is given below:

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

where $q_e$ is the amount of sorbate at time and equilibrium (mg $g^{-1}$), $C_e$ is the equilibrium concentration of the remaining solute in the solution (mg $L^{-1}$), $q_{max}$ is the amount of adsorbate per mass unit of adsorbent at complete monolayer coverage (mg $g^{-1}$), and $K_L$ is the Langmuir equilibrium constant relating to the strength of adsorption (L $mg^{-1}$).

The Freundlich adsorption model (Freundlich, 1906) is given below:

$$q_e = K_L\ C_e^{\frac{1}{n}} \tag{2}$$

where $q_e$ is the amount of sorbate at time and equilibrium (mg g$^{-1}$), $C_e$ is the equilibrium concentration of the remaining solute in the solution (mg L$^{-1}$), $n$ and $K_L$ is the Freundlich equilibrium constant.

The Temkin adsorption model (Temkin, 1941) is given below:

$$q_e = B \ln(\,K_T\ \ C_e) \tag{3}$$

where $q_e$ is the amount of sorbate at time and equilibrium (mg g$^{-1}$), $K_T$ (L mg$^{-1}$) is the Temkin equilibrium constant, $B$ (mg g$^{-1}$) is related with the variation of adsorption energy and $C_e$ is the equilibrium concentration of the remaining solute in the solution (mg L$^{-1}$).

When isotherm arrived at equilibration after 3 days (72 h), the solution was filtered through a Prat Dumas glass microfiber filter (25 mm and retention micrometry 1.2 µm) in order to separate the solid from the liquid phase. So, the liquids were collected in clean vials. The phosphorus concentration was determined using a chromatograph Spectroquant NOVA 60.

### 5.2.4. Batch adsorption experiments

Following other documented experiences (Chen *et al*., 2016; Setter *et al*., 1995), adsorption experiments were carried out in batch mode by using different concentrations of $Na_2HPO_4$ on 50 ml of synthetic wastewater in 100 ml of conical flask and then stirred at different temperatures (283, 293 and 303 K).

Phosphorus stock solution (80 g $L^{-1}$) was prepared by dissolving 0.3704 g $Na_2HPO_4$ in 1 L of distilled water. Further serial dilutions were made to have synthetic wastewater of desired phosphorus concentrations (2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70 and 80 g $L^{-1}$). RA adsorption tests were carried out with doses of 0.5, 1.5, 2.5 and 5 g $L^{-1}$ with a total contact time of 72 h (Figure 14).

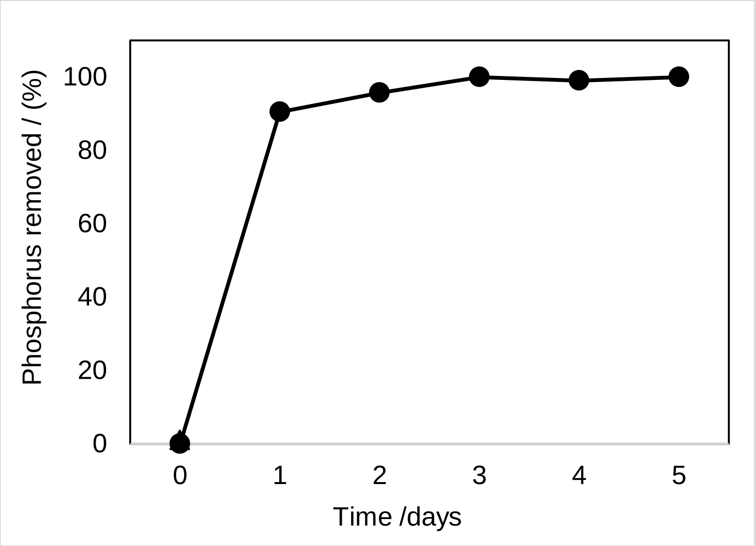

*Fig. 14: Kinetic of reed ash in conical flask with 1.5 g $L^{-1}$ at 293K.*

After adsorption, the solution was filtered through the Prat Dumas glass microfiber filter (25 mm and retention micrometry 1,2 µm). The phosphate concentration was determined using a chromatograph Spectroquant NOVA 60.

The percentage of phosphorus removal (ANEXO 2), or removal efficiency, was calculated by using the formula given below:

$$\% \, Removal \; efficiency = \frac{C_o - C_F}{C_o} \times 100 \qquad (4)$$

where $C_o$ is the initial phosphorus concentration (mg $L^{-1}$) and $C_F$ is the final phosphorus concentration (mg $L^{-1}$).

## 5.3. Results and discussion

### 5.3.1. Physical and chemical characteristics of the adsorbent

The physical and chemical properties of RA are summarized in Table 3. The main component in the adsorbent is silicon oxide with a low concentration of other metal oxides such as iron, aluminium, copper or zinc. However, the amount of alkaline and alkaline-earth metal oxides is very high (Ca and K mainly), approaching that of the silica.

*Table. 3: Physical and chemical properties of the adsorbent materials.*

| Samples | RA |
|---|---|
| pH | 10.3 |
| BET surface area /($m^2$ $g^{-1}$) | 17 |
| External surface area/(%) | 91 |
| Composition/(wt. %) | |
| Si | 25.99 |
| Al | 0.49 |
| Fe | 0.81 |
| Mn | 0.29 |
| Mg | 3.22 |
| Ca | 13.07 |
| Na | 1.04 |
| K | 6.32 |
| P | 1.51 |
| Zn | 0.08 |
| Cu | 0.01 |

The adsorbent has a basic buffer capacity, increasing the pH of water to a value around 10 (see Figure 21). This is due to a high presence of alkaline-earth metal oxides in its composition.

The adsorbent has a high percentage of external surface area, showing that it is not a micro porous material. Hence, it is expected that most of the adsorbent process will take place in that external surface.

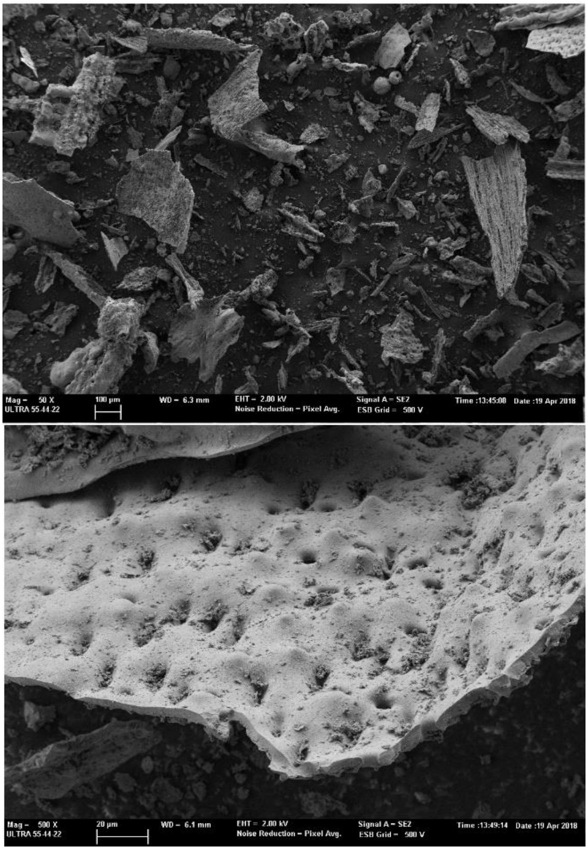

*Fig. 15: Scanning electron micrograph of reed ash adsorbent.*

A scanning electron micrograph (SEM) of the adsorbent (Figure 15) shows a non-crystalline heterogenic distribution of particles in RA; the morphology of the RA indicates the presence of porous and rough surfaces, with different shapes and sizes, in the range from few to a several hundred micrometers.

### 5.3.2. Effect of adsorbent dose

The removal of phosphorus was carried out using synthetic wastewater containing 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70 and 80 g $L^{-1}$ of phosphorus. 110, 130 and 150 g $L^{-1}$ of phosphorus were added to an initial solution of RA-water of 5 g $L^{-1}$ at 293 K temperature. Adsorption isotherm experiments were conducted during a total contact time of 72 h. The results show that the efficiency (mg $g^{-1}$ of P) increases when the contact time between the adsorbent and phosphorus increases, until reaching equilibrium after 48–72 h, as can be seen in Figure 16. This coincides with other experiences (Hoffmann *et al*., 2011).

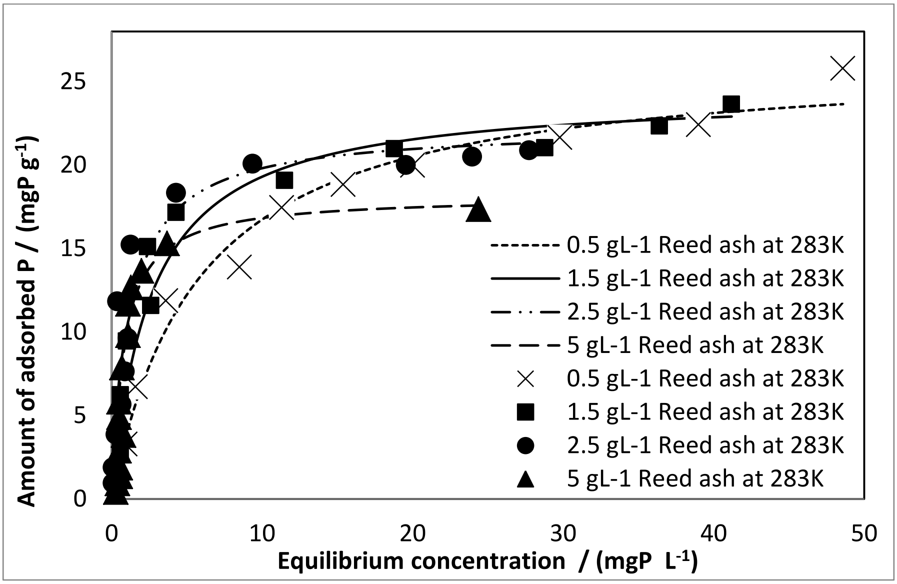

*Fig. 16: Reed ash in conical flask with 0.5, 1.5, 2.5 and 5 g $L^{-1}$ and 2.5, 5, 7.5,10, 15, 20, 25, 30, 40, 50, 60, 65, 70, 75, 80 ppm of phosphorus, at 293 K.*

Adsorption studies of RA were carried out with different doses: 0.5, 1.5, 2.5 and 5 g $L^{-1}$. For RA, the percentage of phosphorus removal varies with the phosphorus–ash ratio (68.0–98.3%). The maximum adsorption (98.3%) is shown by a concentration at 5 g $L^{-1}$ at 293 K. This concentration shows also a high capacity for phosphorus removal (29.3 mg P $g^{-1}$), as can be observed in Figure 17.

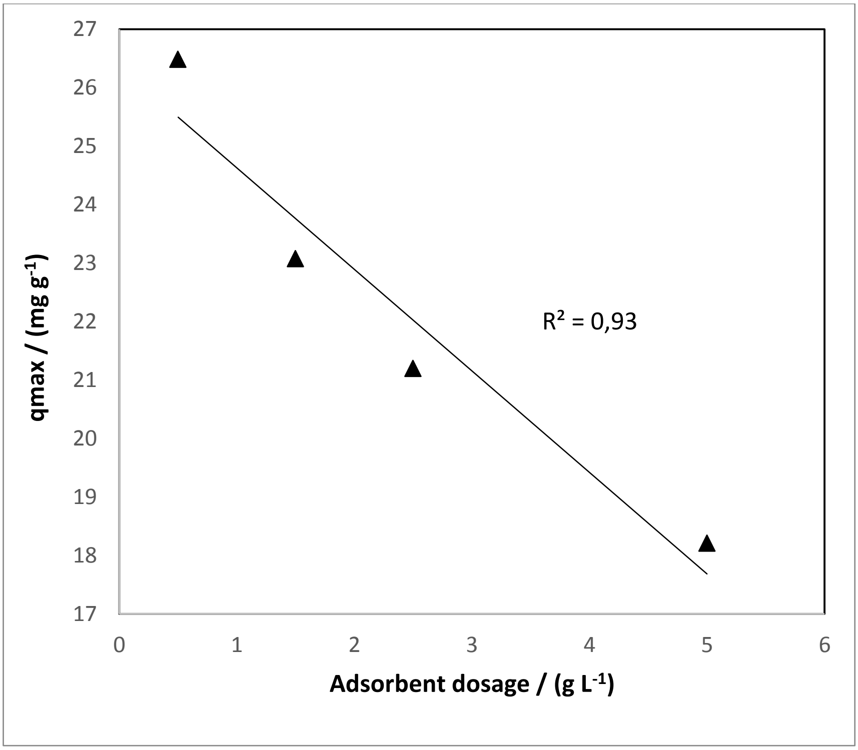

*Fig. 17: Qmax of reed ash in conical flask with 0.5, 1.5, 2.5 and 5 g L*$^{-1}$ *of reed ash at 293K.*

Ion exchange processes can be observed during phosphate adsorption. Water conductivity varies in the range between 286 and 1120 µS cm$^{-1}$ and increases with ash concentration and phosphorus-ash ratio. Thus, the results obtained demonstrate that the phosphorus removal capacity of RA clearly increases when the adsorbent dose increases. This observed relationship coincides with the results of other authors with other plant ashes (Chen *et al*., 2016). With the increasing amount of RA as adsorbent, the decreasing of adsorption capacity was due to the increasing interface area when the suspension was diluted. On the other hand, for the phosphorus adsorption, more ions were into the adsorbent by way of swelling and water absorption by the RA (Ma *et al*., 2011; Vassileva and Voikova, 2009).

### 5.3.3. Influence of temperature on the phosphate removal process

The analysis of the influence of temperature was studied by putting the adsorbent in contact with the phosphorus until reaching equilibrium. This occurs after three days, after which constant values remain. The phosphorus removal was carried out using synthetic wastewater containing different phosphorus concentrations. The experiments were carried out at different temperatures (283, 293 and 303 K) with 1.5 g $L^{-1}$ of RA adsorbent, as shown in Figure 18.

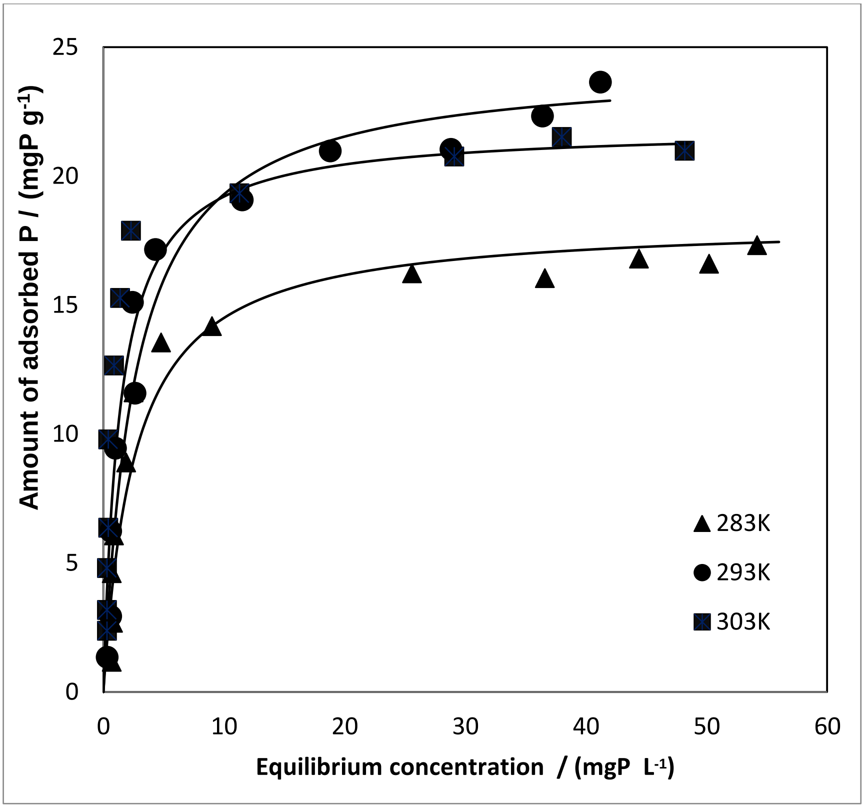

*Fig. 18: Reed ash in conical flask with 1.5 g L$^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 65, 70 and 80 ppm of phosphorus at 283, 293 and 303K.*

Following the Langmuir adsorption model, Figure 19 shows that $q_{max}$ increases when the temperature increases from 283 K (18.22 mg P g$^{-1}$) to 293 K (23.15 mg P g$^{-1}$). Nevertheless, $q_{max}$ decreases when the temperature increases from 293 K (23.15 mg P g$^{-1}$) to 303 K (21.27 mg P g$^{-1}$).

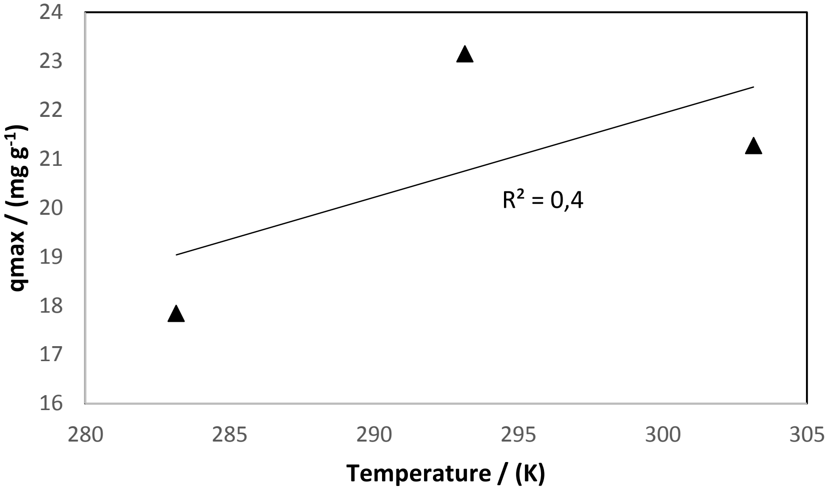

*Fig. 19: Qmax of Reed ash in conical flask with 1.5 g $L^{-1}$ of reed ash at 283, 293 and 303K.*

The effect of adsorption occurs when the value of the isosteric enthalpy is positive. The results between the temperature of 283 K (−2.23 kJ $mol^{-1}$) and 293 K (−1.27 kJ $mol^{-1}$) indicate that the reaction is exothermic. So, when the reaction is exothermic the adsorption increases. On the other hand, the adsorption process decreases from 293 to 303 K (1.07 kJ $mol^{-1}$).

This indicates a negative isosteric enthalpy of adsorption and an endothermic reaction.

Temperature influences significantly the phosphorus removal capacity of RA. Hence, RA with a concentration at 1.5 g $L^{-1}$ and a temperature of 303 K achieves a maximum adsorption of 97.3%.

By contrast, the highest capacity for phosphorus removal (23.15 mg P $g^{-1}$) has been observed with a concentration at 1.5 g $L^{-1}$ at 293 K, as shown in Table 4.

*Table. 4: Isotherm models for adsorption of phosphorus at different temperatures.*

| | | | Reed | |
|---|---|---|---|---|
| Models | T /K | 283 | 293 | 303 |
| Langmuir | $q_{max}$ /(mg $g^{-1}$) | 18,22 | 23,15 | 21,27 |
| | $K_L$ /(L $mg^{-1}$) | 0,39 | 0,59 | 1,53 |
| | $R^2$ | 0.95 | 0.96 | 0.96 |
| | DAIC | 0.0 | | |
| Freundlich | $K_F$* | 4,69 | 9,88 | 11,63 |
| | $n$ | 0,38 | 0,24 | 0,19 |
| | $R^2$ | 0.77 | 0.89 | 0.81 |
| | DAIC | 48.5 | | |
| Tempkin | $B$ (mg $g^{-1}$) | 3,42 | 3,77 | 3,27 |
| | $K_T$ (L $mg^{-1}$) | 4,42 | 12,75 | 28,18 |
| | $R^2$ | 0.89 | 0.94 | 0.67 |
| | DAIC | 24 | | |

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

The Langmuir adsorption model was originally applied to the adsorption of gases on a solid surface and, subsequently, to a liquid phase (Langmuir, 1916). The dynamic adsorption equilibrium 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, and the equilibrium constant (i.e., ratio between adsorption and desorption rate constants) is $K_L$. Taking this into account, $K_L$ is essentially an equilibrium constant of the overall process, which takes place during phosphorus adsorption. Furthermore, its temperature dependence can be used to determine the isosteric enthalpy of adsorption ($\Delta_{ad}H^{o}$) using the Van't Hoff equation:

$$\left(\frac{\partial \, ln \, K}{\partial (1/T)}\right)_{\theta} = -\frac{\Delta_{ad}H^{\circ}}{R} \qquad (5)$$

Figure 20 shows the graphical representation of the Van't Hoff equation of the experimental data. The slope of each curve represents the isosteric enthalpy of adsorption for each adsorbent. A clear linearity of the curves can be observed, as confirmed by the high values of the coefficients of determination ($R^2 > 0.9$) (Figure 20).

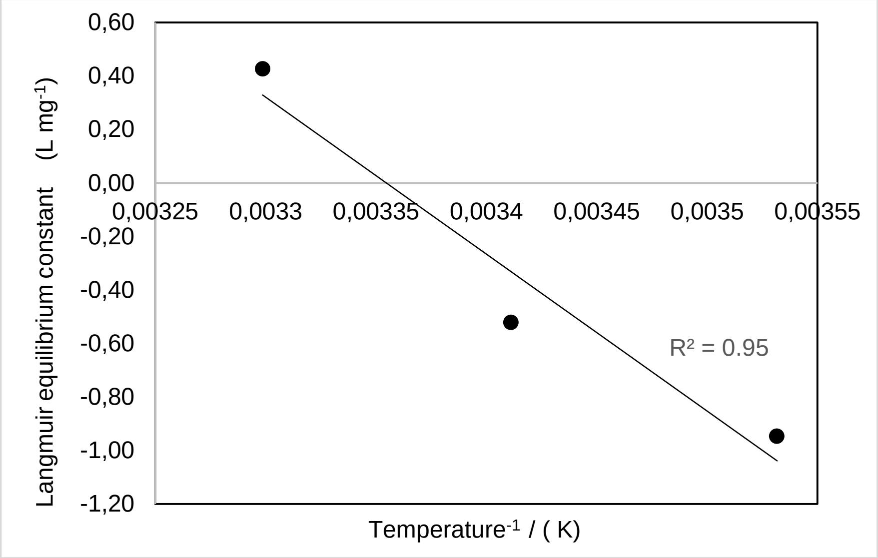

*Fig. 20: Thermodynamic plot for the adsorption of phosphorus at 1/283, 1/ 293 and 1/303 K.*

The calculated enthalpy value of RA is 48.79 kJ mol$^{-1}$. The positive value indicates the endothermic nature of the total process, which takes place during the phosphorus adsorption.

## 5.3.4. Influence of pH on the phosphorus removal process

Different authors studied the influence of the pH on the adsorption capacity of ashes, regulating the pH by means of 0.1 M HCl and 0.1 M NaOH (Mor *et al.*, 2016; Shi *et al.*, 2011). These authors demonstrate that the adsorption increases when the pH decreases. However, other authors conclude for rice husk that a reduction in pH also reduces the absorption capacity (Abbas, 2015).

Furthermore, other research studies reach the final maximum level of absorption capacity around a neutral pH in the case of rice husk and fruit residues (Yadav *et al*., 2015). Consequently, the reference literature shows very different results regarding the influence of pH on the phosphorus absorption capacity by plant ashes.

In the present research, the relation between pHinitial and pHfinal is established. This has been done by adjusting the initial pH values with 0.1 M HCl and 0.1 M NaOH and adding 1.5 g $L^{-1}$ of RA to the aqueous solution. The mixture is stirred until the pH stabilizes. So, pH value is known, as can be observed in Figure 21.

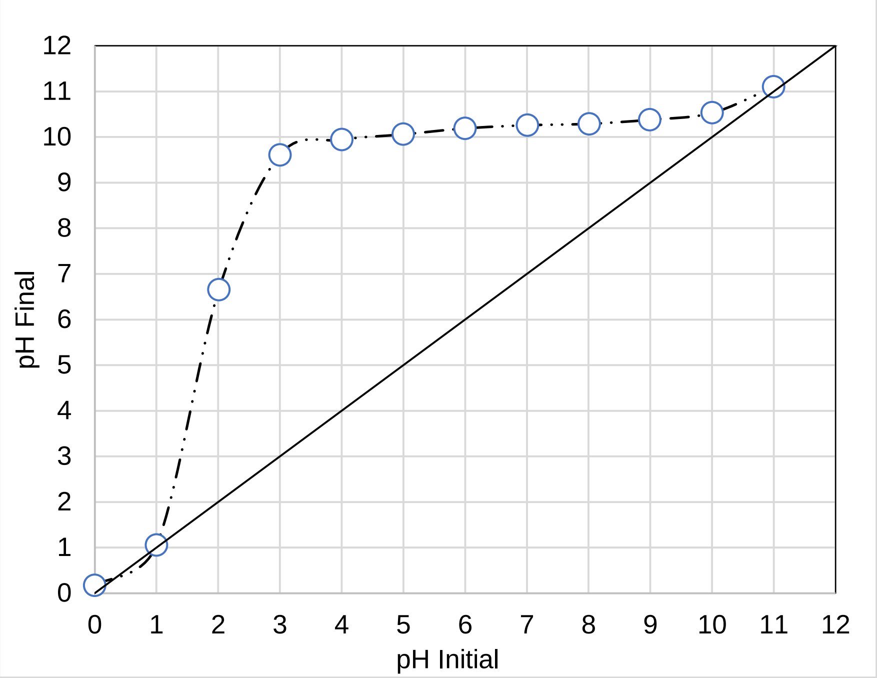

*Fig. 21: Buffer effect of the ash in the pH with 1.5 g $L^{-1}$ of reed ash.*

Figure 21 shows the buffer effect of RA, achieving a pHfinal = 9.61 with pHinitial = 3 and pHfinal = 10.53 with pHinitial = 10.

### 5.3.5. Influence of ionic strength and Ca cations on the phosphate removal process

Figure 22 represents the influence of ionic strength on RA adsorption capacity. The experiments were carried out at 293 K, with a constant adsorbent dose of 10.5 g $L^{-1}$ and different concentrations of phosphorus in the water solution (10-80 mg P $L^{-1}$). The figure allows comparing the behaviour of the original sample (with an average conductivity of 594 $\mu$S $cm^{-1}$) with an alternative test with a controlled ionic strength of 2.0 mS $cm^{-1}$ using the necessary concentration of NaCl. As can be observed, the presence of sodium and chloride ions results in a higher ionic strength. This higher ionic strength has a slight positive effect on phosphorus adsorption capacity. Therefore, the presence of chloride ions does not have negative effect on the adsorption capacity, in line with the conclusions of other authors (Li *et al.*, 2016).

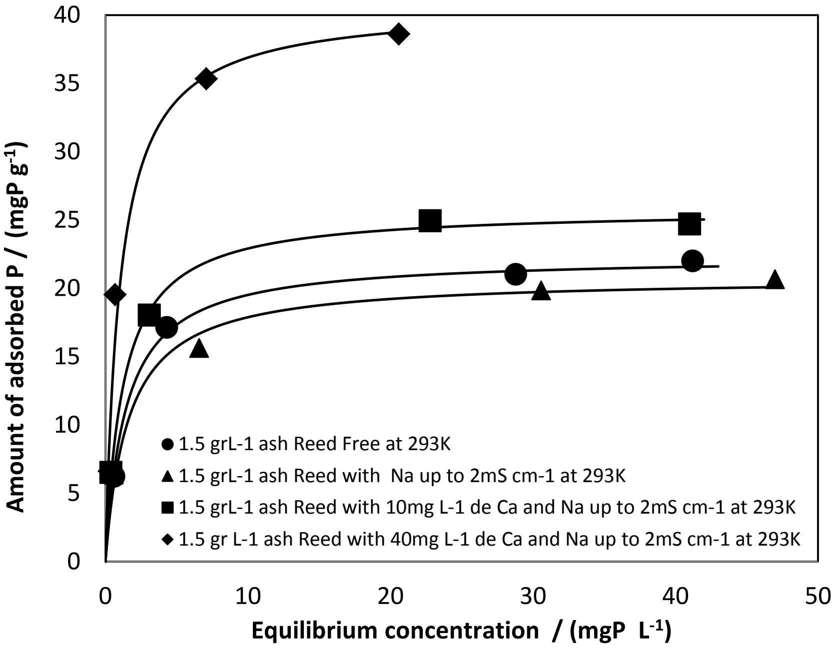

*Fig. 22: Determination of the point of zero charge for reed ash adsorbent.*

The adsorption increase in the presence of sodium and chlorine ions observed in RA can be due to the impediment that supposes a greater ionic strength in the process of exchange / dissolution of ions between the solution and the adsorbent (Wu *et al.*, 2019). This impediment would reduce the presence of other competitive ions of the adsorbent itself in favour of non-competitive chlorine ions.

Following the experiences of other authors (Ahmaruzzaman, 2010; Lu *et al.*, 2009; Ugurlu and Salman, 1998; Vohla *et al.*, 2011), it can be stated that the elimination of phosphorus depends on the dissolution of Ca ions in the adsorbent. These authors also show

that the fixing of phosphorus is mainly carried out by these cations in aqueous solutions with ash. Therefore, for RA it is expected that the higher the Ca content, the greater the phosphorus removal capacity, as observed. To verify the substantive role played by the presence of Ca ions in the solution, the experiments were performed using two different Ca concentrations of $CaCl_2{\cdot}4H_2O$ (10 and 40 mg $L^{-1}$). The tests were performed with a controlled ionic strength of around 2.0 mS $cm^{-1}$ at 293 K, an adsorbent dose of 1.5 g $L^{-1}$ and different concentrations of phosphorus in water (from 10 to 80 mg P $L^{-1}$). Figure 22 shows the results for both Ca concentrations. The presence of Ca in the solution has a positive effect on the capacity of phosphorus adsorption, increasing the capacity as the concentration of Ca increases. These results clearly confirm the determining influence of the Ca cation in the phosphorus removal process.

### 5.3.6. Combined use of reed ash and rice straw ash for phosphorus removal and use as natural fertilizer

Ashes from other plant materials produced by agriculture in the wetlands (specifically RSA) can complement the obtained RA in the removal of phosphorus. Different authors have analysed (Ma *et al*., 2011; Xia *et al*., 2016; Yadav *et al*., 2015) the adsorption capacity of other agricultural waste produced in wetland agriculture, like rice husk, fruit juice residues and wheat straw. Taking into account that rice is the most extended agricultural crop in wetlands worldwide, a combined use of RA and RSA as a natural phosphorus filter can be an interesting alternative, leading to a revaluation of these residues (Soria, 2006; Wong *et al*., 2013).

In order to compare with the previous results, the experiments have been conducted with a constant ash concentration of 5 g $L^{-1}$ in the aqueous solution and a constant temperature of 293 K. Furthermore, to compare different ash mixtures, the following ratios between RA and RSA have been tested: 5:0, 4:1, 3:2, 2:3, 1:4, 0:5. The phosphorus concentrations are 5, 10, 20, 40, 60 and 80 mg $L^{-1}$. An additional test has been conducted with 110 g $L^{-1}$ of phosphorus concentration for the mixture RA and RSA 5:0.

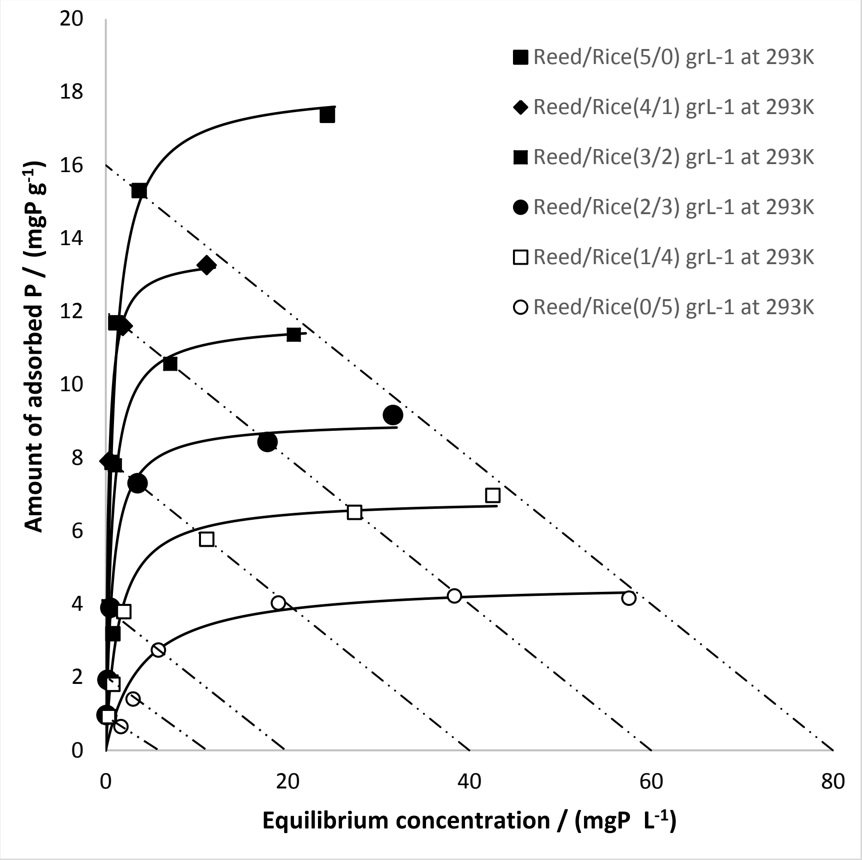

*Fig. 23: Proportional adsorption mixing rice straw ash and reed ash in conical flask with 5 g $L^{-1}$ and 5, 10, 20, 40, 60 and 80 g $L^{-1}$ of phosphorus, at 293 K. On relation between Reed/Rice 5/0, in addition there are 110 g $L^{-1}$ of phosphorus.*

Figure 23 shows the obtained results of these experiments. The curves obtained for the different RA and RSA ash mixtures show that the phosphate adsorption is proportional to the amounts of adsorbents in the different mixtures.

For the same amount of initial phosphorus in the aqueous solution, a linear function is generated with which the intermediate points that are between the pure concentrations of each adsorbent can be calculated. This function is given by the equation:

$$q_e = \frac{[P_O]}{A} - \frac{V \times C_e}{A} \qquad (6)$$

where $q_e$ is the amount of sorbate at time and equilibrium (mg $g^{-1}$), V is the volume (L), A is the amount of total ash mixed (g), $C_e$ is the equilibrium concentration (mg $L^{-1}$) and $P_o$ is the initial amount of phosphorus (mg $L^{-1}$).

Supplies of rice straw and reed straw are readily available; different studies recommend the use of rice straw and reed straw as biomass for producing energy in biomass plants (Delivand *et al.*, 2011; Važić *et al.*, 2015). The results of another study concludes that crop biomass ash can be an adequate phosphorus source comparable to that of highly soluble commercial phosphorus fertilizer (Schiemenz and Eichler-Löbermann, 2010). In addition, it has been shown that different crop biomass ashes, i.e. rape meal ash, straw ash, and cereal ash, could be used as fertilizer. While other studies show the capacity of adsorption of cereal straw (Mor *et al.*, 2016) and the adsorption of heavy metals or dyes of reed straw (Ahmed, 2017).

Rice fields and wetlands generate a significant amount of non-agricultural biomass, reed straw generally, and considering that in different places there are different proportions of rice straw waste and non-agricultural biomass production, therefore, the use of mixtures of rice and reed straw was studied. The proportions of the mixtures depends on the availability of reed and rice ashes, the initial phosphorus concentration and the final phosphorus concentration in the water. In the case of rice and reed, the higher the amount of RA, the greater the adsorption capacity.

## 5.4. Conclusions

Reed is a natural biomass which is available in large quantities and can be used to produce energy in biomass power plants. These companies generate a waste called RA, which can be used to remove phosphorus from contaminated water. The results of this study demonstrate the adsorption capacity of phosphorus and show that the maximum adsorption capacity is up to 98.3%, in a concentration at 5 g $L^{-1}$ at 293 K. This concentration also shows a high capacity for phosphorus removal ($q_{max}$ 29.3 mg P $g^{-1}$). The Langmuir isotherms model depicts the best fits to the experimental data with correlation coefficients greater than 0.95. The adsorption

of phosphorus ions in the RA adsorbent is a rapid process, less than 72 h. SEM of the adsorbent shows non-crystalline particles and the morphology of RA indicates the presence of a porous and rough surface. The results of the study indicate that the RA could be used as a low-cost adsorbent for the treatment of water and wastewater treatment.

# 6. CAPITULO III: REDUCCIÓN DE FÓSFORO DE AGUAS RESIDUALES A TRAVÉS DE PROCESOS DE ADSORCIÓN REUTILIZANDO CENIZA DE MADERA Y PAJA PRODUCIDA EN INSTALACIONES DE BIOENERGÍA. *REDUCTION OF PHOSPHORUS FROM WASTEWATER THROUGH ADSORPTION PROCESSES REUSING WOOD AND STRAW ASH PRODUCED IN BIOENERGY FACILITIES.*

# CAPITULO III

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# 6. CAPITULO III: REDUCCIÓN DE FÓSFORO DE AGUAS RESIDUALES A TRAVÉS DE PROCESOS DE ADSORCIÓN REUTILIZANDO CENIZA DE MADERA Y PAJA PRODUCIDA EN INSTALACIONES DE BIOENERGÍA. *REDUCTION OF PHOSPHORUS FROM WASTEWATER THROUGH ADSORPTION PROCESSES REUSING WOOD AND STRAW ASH PRODUCED IN BIOENERGY FACILITIES.*

## 6.1. Introduction

The high content of phosphorus and nitrogen in bodies of water that proceeds from wastewater and agricultural fertilization leachate generates problems of eutrophication in rivers, lakes (García-Nieto *et al.*, 2016) and lagoons (Martín *et al.*, 2013; Soria *et al.*, 1987).

The European Union is determined to improve the quality of its water bodies, for instance through the removal of phosphorus, which causes eutrophication (European Union, 1991) . At the same time, the EU is interested in reusing its critical raw materials, such as phosphorus, within a circular economy perspective (Gislev *et al.*, 2018). Hence, it is important to make a correct use of this mineral, as well as reuse the phosphorus contained in wastewater.

The EU has emitted several directives in this respect. According to the European Directive 91/271/CEE, the limit values of phosphorus in bodies of water are 2 mg $L^{-1}$ in agglomerations of between 10,000 and 100,000 population equivalent and 1 mg $L^{-1}$ in larger agglomerations (European Union, 1991). Also, the European Directive 2009/28/EC has established that by 2020 at least 20% of primary energy consumption should come from renewable sources (European Union, 2009).

The production of cereal occupies a third of the cultivable surface within the European Union (European Union, 2014). For example, in Spain, 2,122,000 ha of wheat and 3,177,000 ha of barley are produced (Schils *et al*., 2018). Furthermore, in different regions of Spain, the culture of using cereal residual biomass in order to generate alternative energy is being implemented (García-Maraver *et al*., 2012; Ortiz de Zárate *et al*., 2005; Santamarta *et al*., 2014; Ubeda Delgado and Antolín Giraldo, 1995).

Additionally, an effective way of producing renewable energy is to use wood from plantations or forests, reducing dependence on fossil fuels (Deboni *et al*., 2018). For example, *Paulownia spp*. plantations are being cultivated in different countries to produce biomass for the generation of energy (Fernández-Puratich *et al*., 2014; Senelwa and Sims, 1999). They are also being grown to produce energy crops (Fernández-Puratich *et al*., 2014; Krasuska *et al*., 2010; Zegada-Lizarazu *et al*., 2010), due to the rapid growth.

One of the main technical problems for energy production through biomass is the generation of waste, such as fly ash (Ortiz de Zárate *et al*., 2005). Biomass ashes can find applications in agriculture as fertilizer (Ingerslev *et al*., 2011), as well as in adsorption processes (Ahmaruzzaman, 2010; Girón *et al*., 2013).

Phosphorus in water can be eliminated by adsorption with different biomass ashes (Mor *et al*., 2016). Adsorption is a process by which atoms, ions or phosphorus molecules (adsorbate) dissolved in water are retained on the solid surface of a material, in this case one of the three ashes (adsorbent).

Various scientific articles have detailed different ways of performing adsorption with biomasses, for instance the adsorption of phosphorus with rice husk (Mor *et al*., 2016), the adsorption of phosphorus with resins made of wheat (Liu *et al*., 2013) or the adsorption of nickel with barley (Thevannan *et al*., 2010).

Taking into account the actual state of the art, the research aims to study the elimination of phosphorus from wastewater through adsorption processes, for reducing the eutrophication problems present in the L’Albufera Lagoon in València, reusing ash waste produced in biomass plants. The materials wheat straw ash (WSA), barley straw ash (BSA) and paulownia wood ash (PWA) are produced in biomass plants in rural areas. This biomass plants are supplied by fast-growing forest plantations for producing energy crops with as well as from residues of sylvicultural treatments (thinning or pruning). To do this, batch-type experiments using WSA, BSA and PWA allow the analysis of the effect of several parameters on the removal of phosphorus from wastewater, that is contact time, phosphate-ash ratio, ash dose and temperature.

## 6.2. Materials and methods

### 6.2.1. Preparation and characterization of adsorbents

Wheat straw was obtained from wheat fields of Ademuz (Spain), geographical coordinates: 40° 2'11.29"N, 1°18'6.37"W. Barley straw was obtained from barley fields of Ademuz (Spain), geographical coordinates: 40° 2'27.07"N, 1°18'11.60"W. Paulownia was obtained from wood production fields of Paiporta (Spain), geographical coordinates: 39°25'25.13"N, 0°26'19.72"W. After combustion in a bioenergy plant located in Ademuz (Spain), the three ashes were heated at 823 K for 1 h in muffle furnaces; the WSA and PWA lost around 25% of weight, the BSA lost around 15% of weight.

Thereafter, each ash was washed with distilled water until the electric conductivity was less than 1 mS $cm^{-1}$. Following Mor *et al.*

(2016), the ashes were dried at 378 K in an oven for 24 h to achieve constant weight and sieved again to ensure uniform particle size. Characterization of adsorbents was done using different techniques. Nitrogen concentration was determined through the Kjeldahl method (AOAC, 2000) using a Kjeltec 2100 Distillation Unit (FossTecator, Högamäs, Sweden). For the analyses of minerals, 2 g of the ashes was then dissolved in 2 mL of concentrated HCl. The mixtures were heated until the first vapours appeared, and immediately distilled water (2–3 mL) was added. Subsequently, the mixtures were filtered using an ash-free filter and the extracts were brought up to 100 mL with distilled water. K and Na were analysed by flame photometry using a Jenway PFP7 (UK) flame photometer, and the rest of the minerals (Al, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, P, Si and Zn) were analysed by inductively coupled plasma optical emission spectrometry (Agilent 700 Series ICP Optical Emission Spectrometer). Multi-element calibration standards were prepared with specific concentrations of the different elements. Table 5 shows the wavelength values used in each determination and the range of the calibration line used.

Carbon concentration was determined through the Walkley and Black method (Walkley and Black, 1934) based on the Schollenberger method (Schollenberger and Simon, 1945).

The pH determination of the samples was determined in the aqueous extract 1:5 (ash:water) using a Crison pH&Ion-Meter GLP

22+. The electrical conductivity measurement was determined in the aqueous extract 1:5 (ash:water) using a conductometer WTW Multi 340i.

Three replicates were analysed for every sample; the concentration values used were the mean of the three readings.

*Table. 5: Elements, wavelength values and the range of the calibration line.*

| Element | Wavelength (nm) | Range of the calibration line (ppm) |
|---|---|---|
| Al | 396.152 | 0-5 |
| Ca | 317.933 | 0-50 |
| Cd | 214.439 | 0-1 |
| Co | 228.615 | 0-1 |
| Cr | 267.716 | 0-1 |
| Cu | 324.754 | 0-1 |
| Fe | 259.940 | 0-5 |
| K | 766.491 | 0-50 |
| Li | 460.289 | 0-1 |
| Mg | 285.213 | 0-10 |
| Mn | 257.610 | 0-1 |
| Na | 590.000 | 0-10 |
| Ni | 231.604 | 0-1 |
| P | 177.434 | 0-10 |
| Si | 288.158 | 0-50 |
| Zn | 213.857 | 0-1 |

The particle morphology of the samples was studied by field emission scanning electron microscopy (FESEM), using a ZEISS Ultra5-55 microscope. Moreover, textural properties were determined by $N_2$ adsorption-desorption isotherms measured on a Micromeritics ASAP 2020 at 77 K.

### 6.2.2. Adsorption isotherms and kinetics: effect of the time on the adsorbent

Adsorption isotherm experiments following Langmuir (1916), Freundlich (1906) and Temkin (1941) were conducted varying contact time from 0 to 120 h with initial phosphorus concentration of 80 mg $L^{-1}$ for PWA and WSA, and 90 mg $L^{-1}$ for BSA at different temperatures (283 K, 293 K and 303 K).

The Langmuir adsorption (Langmuir, 1916) is:

$$q_e = \frac{q_{max}\, K_L C_e}{1+K_L C_e} \qquad (1)$$

where qe is the amount of sorbate at time and equilibrium (mg $g^{-1}$), Ce is the equilibrium concentration of the remaining solute in the solution (mg $L^{-1}$), qmax is the amount of adsorbate per mass unit of adsorbent at complete monolayer coverage (mg $g^{-1}$) and KL is the Langmuir equilibrium constant relating to the strength of adsorption (L $mg^{-1}$).

The Freundlich (Freundlich, 1906) is:

$$q_e = K_L\, C_e^{\frac{1}{n}} \qquad (2)$$

where $q_e$ is the amount of sorbate at time and equilibrium (mg $g^{-1}$), $C_e$ is the equilibrium concentration of the remaining solute in the solution (mg $L^{-1}$), $n$ and $K_L$ is the Freundlich equilibrium constant.

The Temkin (Temkin, 1941) is:

$$q_e = B \ln( K_T \ \ C_e) \qquad (3)$$

where $q_e$ is the amount of sorbate at time and equilibrium (mg $g^{-1}$), *KT* (L mg$^{-1}$) is the Temkin equilibrium constant and B (mg $g^{-1}$) is related with the variation of adsorption energy and $C_e$ is the equilibrium concentration of the remaining solute in the solution (mg $L^{-1}$).

The model that best adapts to the isotherms of adsorption is the model of Langmuir, in adsorptions of equivalent ions and monolayer on the surface of the adsorbent (Ahmaruzzaman, 2010; Seliem *et al.*, 2016).

When isotherm arrived at equilibration in WSA, BSA and PWAat 4 days (96 h), the solution was filtered through a Prat Dumas glass microfiber filter (25 mm and retention micrometry 1.2 µm) to separate the solid from liquid phase. The liquids were collected in clean vials. The concentration of phosphorus was determined using a chromatograph Spectroquant NOVA 60. Figure 24 shows the time that the kinetic needs to reach the equilibrium.

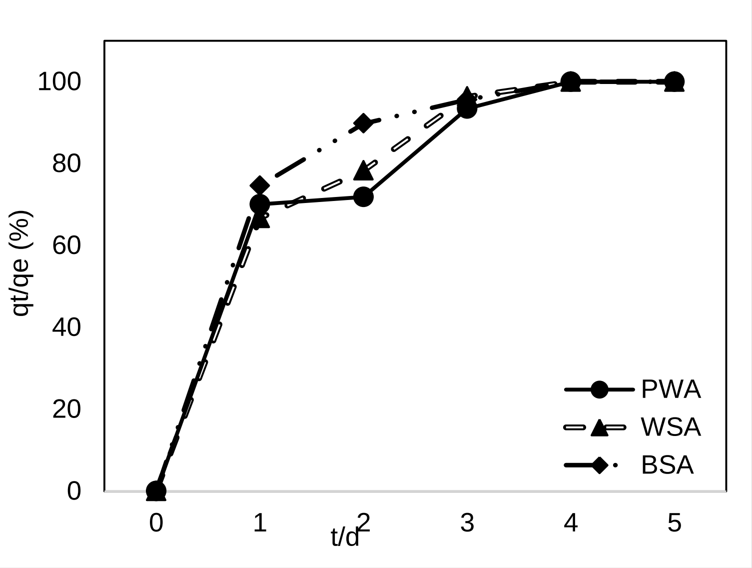

*Fig. 24: Kinetic of PWA, WSA ash and BSA ash in conical flask at 293 K.*

### 6.2.3. Batch adsorption experiments

Adsorption experiments were carried out in batch mode by using different concentrations of sodium hydrogen phosphate ($Na_2HPO_4$) on 50 ml of synthetic wastewater in 100 ml of conical flask and then stirred at 283 K, 293 K, 303K of temperature.

Phosphorus stock solution (80 mg $L^{-1}$) was prepared by dissolving 0.3704 g sodium hydrogen phosphate ($Na_2HPO_4$) in 1 L of distilled water. Further serial dilutions were made to have synthetic wastewater of desired phosphorus concentration (2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70 and 80 mg $L^{-1}$).

Adsorption studies for PWA were carried out with doses 1.5 g $L^{-1}$, 2.5 g $L^{-1}$ and 5 g $L^{-1}$, for BSA and WSA with 2.5 g $L^{-1}$, 5 g $L^{-1}$ and 10 g $L^{-1}$, all having contact time of 96 h. After adsorption, the solution was filtered through the Prat Dumas glass microfiber filter (25 mm and retention micrometry 1.2 µm) and phosphorus concentration was determined using a chromatograph Spectroquant NOVA 60.

The percentage removal of phosphorus (Fig. 24 and ANEXO 3) was calculated by using the following formula:

$$\%\, Removal\ efficiency = \frac{C_o - C_F}{C_o} \times 100 \qquad (4)$$

$C_o$ is the initial concentration (mg $L^{-1}$) and $C_F$ is the final concentration of phosphorus (mg $L^{-1}$).

## 6.3. Results and discussion

### 6.3.1. Characterization of adsorbent

The characterization of the different ashes is summarized in Table 6. It can be seen that alkaline earth is the main component in the adsorbents principally calcium and magnesium. In addition, alkalines are present, the main elements being potassium and sodium. There are other metal oxides such as aluminium, iron or copper.

This fact agrees with the contribution of nutrients to the soil by the straw ashes that had been described by Ribó *et al*. (2017). The low percentage of carbon indicates that these materials are essentially inorganic.

*Table. 6: Physical and chemical properties of the adsorbent materials.*

| Samples | WSA | BSA | PWA |
|---|---|---|---|
| $pH_{PZC}$ | 11.89 | 11.49 | 11.00 |
| Elementary analysis/(wt. %) | | | |
| Carbon | 1.102 | 0.938 | 0.818 |
| Nitrogen | 0.034 | 0.042 | 0.025 |
| Composition/(wt. %) | | | |
| Si | 0.481 | 0.144 | 0.213 |
| Al | 1.526 | 0.282 | 0.232 |
| Fe | 1.020 | 0.228 | 0.150 |
| Mn | 0.041 | 0.022 | 0.012 |
| Mg | 2.423 | 2.541 | 1.459 |
| Ca | 17.140 | 8.220 | 6.360 |
| Na | 1.299 | 1.263 | 2.559 |
| K | 3.474 | 6.527 | 3.064 |
| P | 1.961 | 1.235 | 1.173 |
| Zn | 0.106 | 0.013 | 0.005 |
| Cu | 0.0393 | 0.0030 | 0.0036 |
| Li | 0.0051 | n.d | n.d |
| Ni | 0.0010 | n.d | 0.0019 |
| Co | n.d | n.d | 0.0030 |
| Cd | n.d | n.d | n.d |
| Cr | 0.00073 | n.d. | n.d |

n.d. not detected

Moreover, the scanning electron micrograph of the adsorbents shows materials with different shapes, sizes and structures are non-crystalline with a heterogenic distribution of particles in the materials (see Fig. 25).

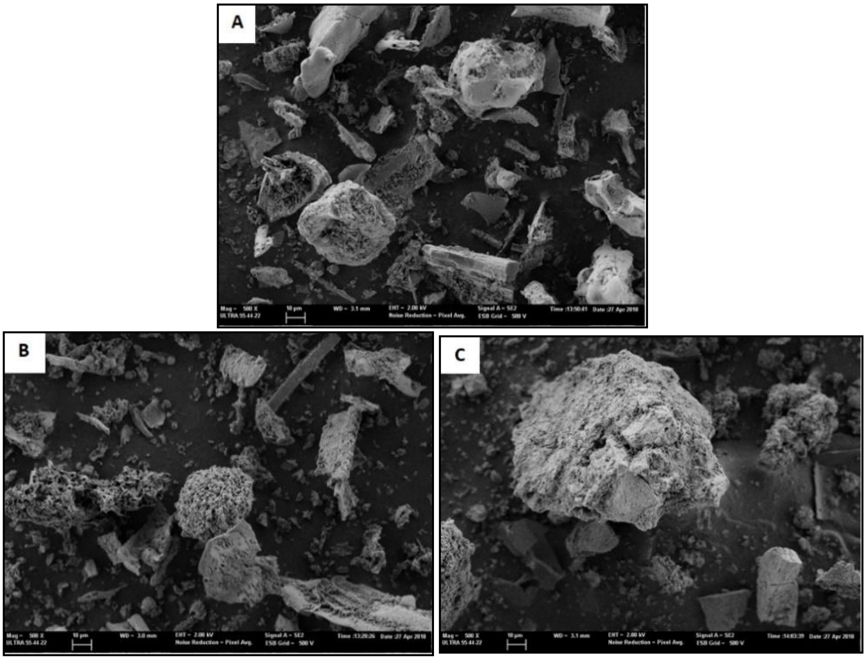

*Fig. 25: Scanning electron micrograph of WSA (A), BSA (B) and PWA (C) adsorbents.*

### 6.3.2. Effect of adsorbent dose

The removal of phosphorus was carried out using synthetic wastewater containing 2.5, 5, 7.5, 10, 15, 20, 25, 30, 40, 50, 60, 65, 70, 75 and 80 mg $L^{-1}$ of phosphorus.

Adsorption isotherm experiments were conducted during contact time 96 h. The results obtained show that the amount of phosphorus-removed increases with increasing the adsorbent dosage (see Fig. 26) and during the adsorption process until reaching the equilibrium. This behaviour was also observed by Chen *et al*., 2016.

In the case of the PWA, the percentage of phosphorus removal varies with the phosphorus-ash ratio (24.84–98.80%). With the WSA, the percentage of phosphorus removal varies with the phosphorus-ash ratio (28.58–94.61%), and with the BSA, the percentage of phosphorus removal varies with the phosphorus-ash ratio (42.29–98.49%).

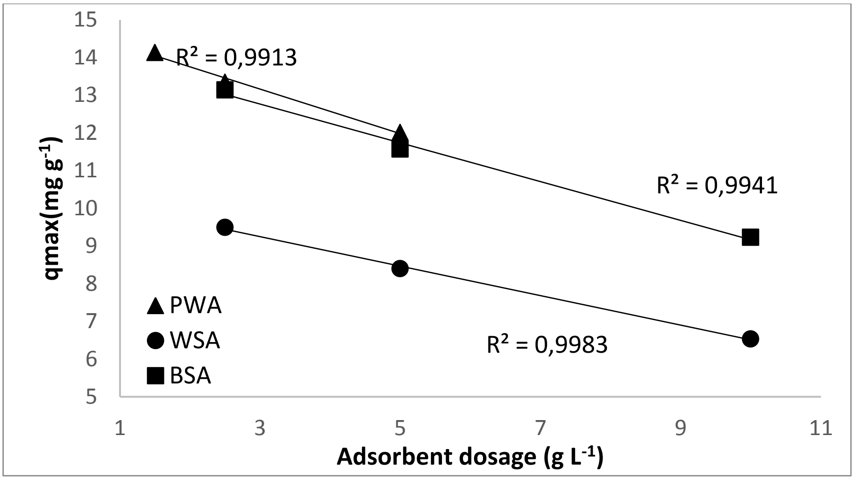

*Fig. 26: qmax of WSA and BSA in conical flask with 2.5, 5 and 10 g $L^{-1}$ and qmax of PWA in conical flask with 1.5, 2.5 and 5 g $L^{-1}$, at 293 K*

Figure 27 shows that PWA achieves the maximum adsorption (98.80%) with a concentration at 5 g $L^{-1}$ and 293 K. A high capacity for phosphorus removal (13.18 mg P $g^{-1}$) has been observed with a concentration at 1.5 g $L^{-1}$ and 293 K. An ion exchange process has been observed during phosphorus adsorption. Water conductivity varies in the range 271-921 μS $cm^{-1}$ and increases with ash concentration and phosphate-ash ratio, as demonstrated by (Kawakita *et al*., 2008).

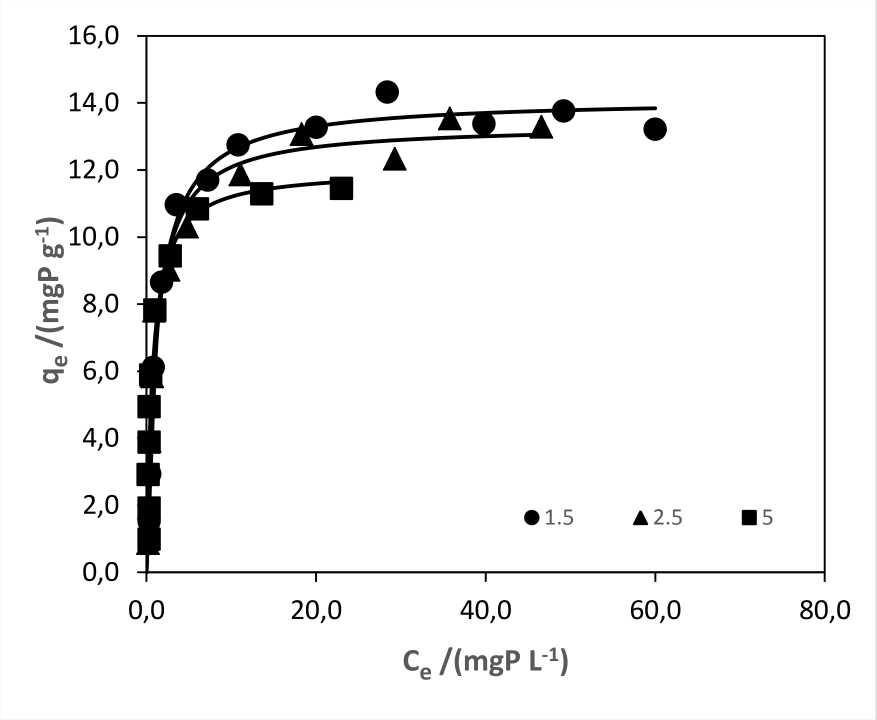

*Fig. 27: PWA in conical flask with 1.5, 2.5 and 5 g $L^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 65, 70 and 80 mg $L^{-1}$ of phosphorus, at 293 K.*

Furthermore, Fig. 28 shows that WSA shows maximum adsorption (94.61%) with a concentration at 10 g $L^{-1}$ and 293 K. A high capacity for phosphate removal (9.14 mg P $g^{-1}$) has been observed with a concentration at 2.5 g $L^{-1}$ and 293 K.

An ion exchange process has been observed during phosphorus adsorption. Water conductivity varies in the range 470–1413 µS $cm^{-1}$ and increases with ash concentration and phosphorus-ash ratio (Kawakita *et al.*, 2008).

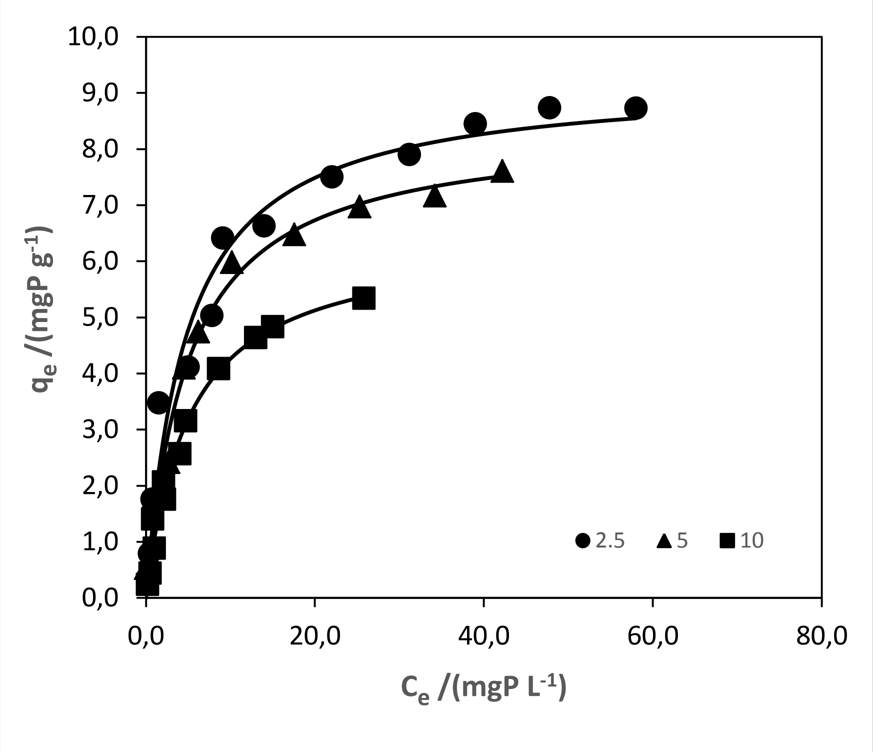

*Fig. 28: WSA in conical flask with 2.5, 5 and 10 g $L^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 65, 70 and 80 mg $L^{-1}$ of phosphorus, at 293 K*

Moreover, Fig. 29 shows that BSA with a concentration at 10 g $L^{-1}$ and 293 K shows maximum adsorption at 98.49%. A high capacity for phosphorus removal (13.52 mg P $g^{-1}$) has been observed with a concentration at 2.5 g $L^{-1}$ and 293 K. An ion exchange process has been observed during phosphorus adsorption. Water conductivity varies in the range 366–1214 µS $cm^{-1}$ and increases with ash concentration and phosphorus-ash ratio (Kawakita *et al*., 2008).

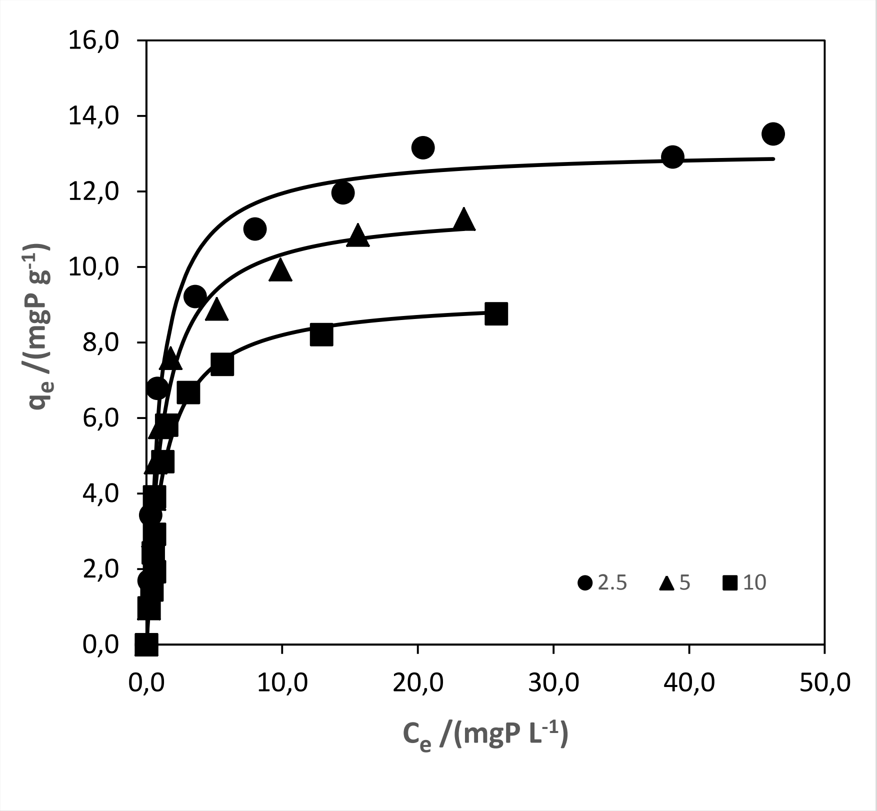

*Fig. 29: BSA ash in conical flask with 2.5, 5 and 10 g $L^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 65, 70 and 80 $mgL^{-1}$ of phosphorus, at 293 K.*

Finally, PWA, BSA and WSA data indicates that the adsorbed amount of phosphorus increased with the increasing dose (g $L^{-1}$) of adsorbent. Thus, with the increasing adsorbent amount, the decreasing adsorption capacity was due to the increasing interface area. But for the adsorption of phosphorus, more ions went into the

adsorbent by way of swelling and water absorption by the adsorbent. So, when the ash dose was increased, an increase in phosphorus removal was also observed, as some other authors have also documented for other ash materials (Ma *et al.*, 2011; Vassileva and Voikova, 2009).

### 6.3.3. Phosphorus adsorption isotherms. Effect of temperature.

The temperatures of 283 K, 293 K and 303 K were chosen because the temperature of wastewater coming to rivers and lagoons in the Mediterranean area are normally within these chosen ranges. Martín *et al*. (2013) measured average temperatures of 291.75 K In another study, (Soria, 2006) measured average temperatures of 291.85 ± 6.9 K for the period between 1986 and 1998 and 292.55 ± 6.2 K for the period between 1997 and 2000.

The study of the effects of temperature was carried out. The adsorbent contacts with the phosphorus until reaching a constant equilibrium, which happens after 4 days (96 h). The removal of phosphorus was carried out using synthetic wastewater containing 2.5, 5, 7.5, 10, 15, 20, 25, 30, 40, 50, 60, 65, 70, 75 and 80 mg $L^{-1}$ of phosphorus Figure 30 shows the qmax of the three materials considering that the experiments were conducted at different temperatures (283 K, 293 K and 303 K) with 5 g $L^{-1}$ for WSA and BSA and 2.5 g $L^{-1}$ for PWA.

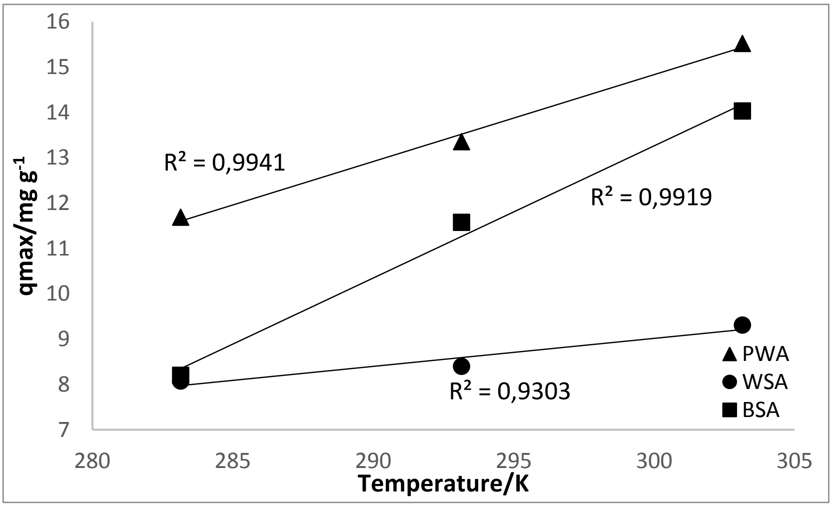

*Fig. 30: qmax of WSA and BSA ash in conical flask with 5 g $L^{-1}$ and qmax of PWA ash in conical flask with 2.5 g $L^{-1}$, at 283, 293 and 303 K.*

The adsorption isotherms were carried out with the same amounts of phosphorus so as not to vary the electrical conductivity of the solution, because of this the amounts of adsorbent vary so that the adsorption isotherm reaches equilibrium.

The obtained results demonstrate for PSA that the temperature increases the phosphorus removal from 96.99 to 97.31%, with a concentration at 2.5 g $L^{-1}$ and 303 K. Figure 31 shows the maximum adsorption at 97.31%. The best capacity for phosphorus removal (15.7 mg P $g^{-1}$) was observed with a concentration at 2.5 g $L^{-1}$ and 303 K for PSA. Water conductivity varied in the range of 361-738 µS $cm^{-1}$ and increases with the temperature, similar to other authors (Mor *et al*., 2016).

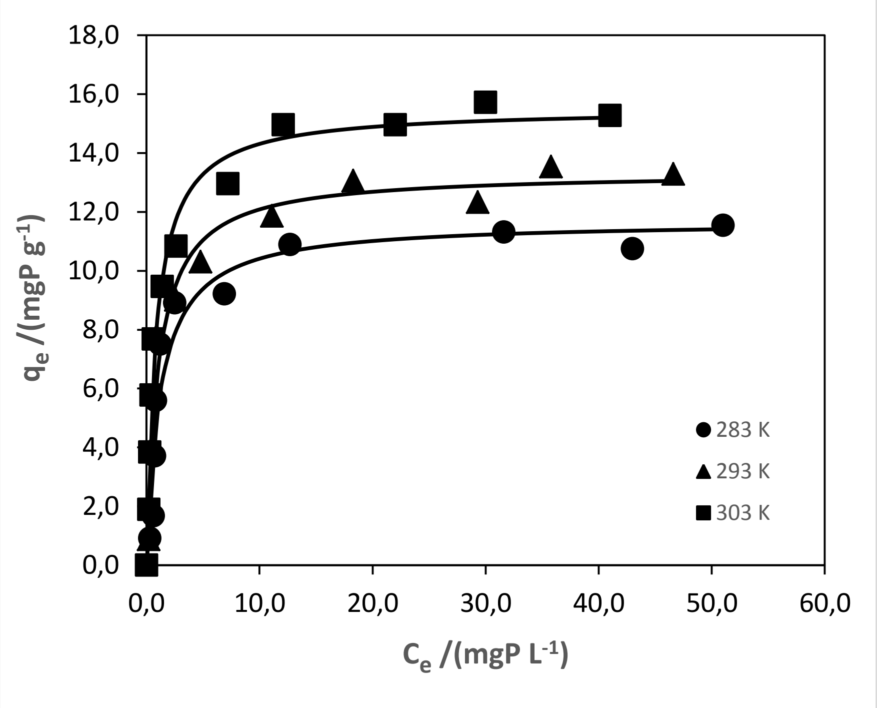

*Fig. 31: PWA in conical flask with 2.5 g $L^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 mg $L^{-1}$ of phosphorus, at 283, 293 and 303 K.*

Furthermore, for WSA, the temperature increases the phosphorus removal from 83.05 to 93.94%, with a concentration at 5 g $L^{-1}$ and 303 K. The maximum adsorption is at 93.94%, as shown in Fig. 32. The worst capacity for phosphorus removal (9.57 mg P $g^{-1}$) has been observed with a concentration at 5 g $L^{-1}$ and 303 K for WSA. Water conductivity varies in the range 676–1147 µS $cm^{-1}$ and increases with the temperature. This behaviour is also observed by El-Naas *et al*. (2010) and Mor *et al*. (2016).

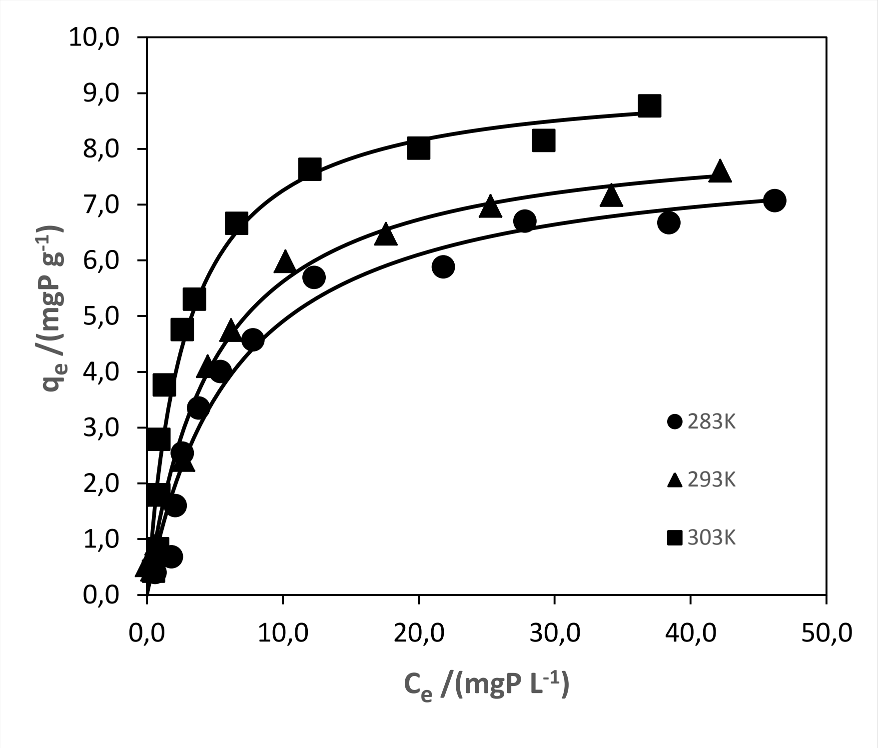

*Fig. 32: WSA in conical flask with 5 g $L^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 mg $L^{-1}$ of phosphorus, at 283, 293 and 303 K.*

Moreover, for BSA, the temperature increases from 95.85 to 97.5% the phosphorus removal, with a concentration at 5 g $L^{-1}$ and 303 K. Figure 33 shows the maximum adsorption at 97.5%. The second best capacity for phosphorus removal (13.06 mg P $g^{-1}$) has been observed with a concentration at 5 g $L^{-1}$ and 303 K for BSA. Water conductivity varies in the range 725–997 µS $cm^{-1}$ and increases with the temperature, following also the results obtained by Mor *et al*. (2016).

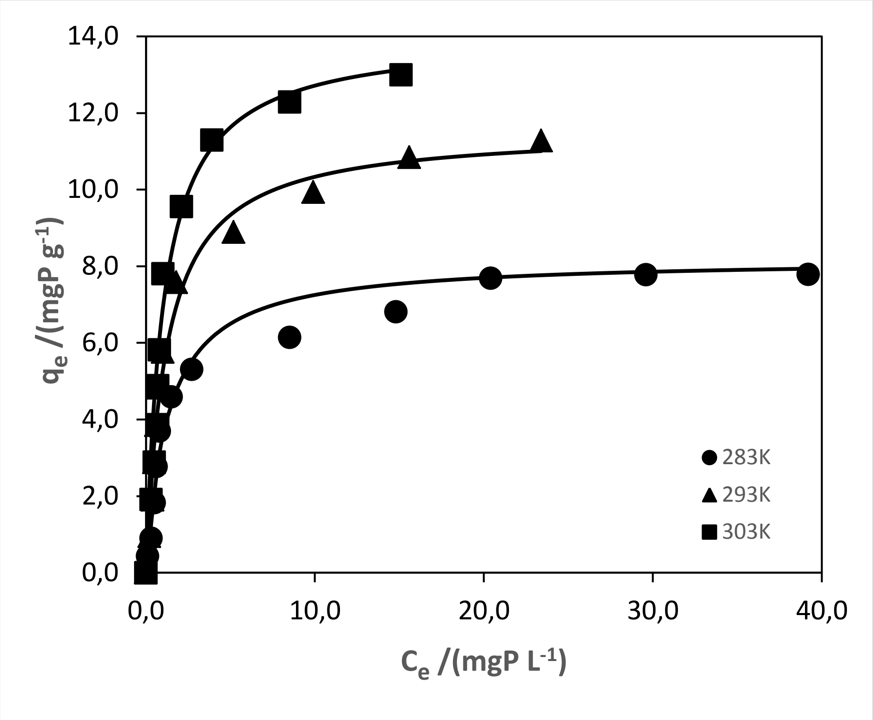

*Fig. 33: BSA in conical flask with 5 g $L^{-1}$ and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 mg $L^{-1}$ of phosphorus, at 283, 293 and 303 K.*

Table 7 summarizes the isotherm models for adsorption of phosphorus for the three ashes at the different temperatures tested. Consequently, PWA, BSA and WSA data indicate that adsorption increases when temperature increases. This finding matches other studies that confirm that increasing the temperature increases the adsorption efficiency (El-Naas *et al*., 2010; Mor *et al*., 2016).

In addition, Table 7 shows the fitted parameters of the three studied isotherm models, including coefficients of determination

($R^2$). According to the data obtained, Freundlich isotherm model presents the worst value $R^2$ in all cases. 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. 7: Isotherm models for adsorption of phosphorus for three materials at different temperatures.*

| | | Paulownia | | | Wheat | | | Barley | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Models | T /K | 283 | 293 | 303 | 283 | 293 | 303 | 283 | 293 | 303 |
| Langmuir | $q_{max}$ /(mg g$^{-1}$) | 11.68 | 13.34 | 15.51 | 8.07 | 8.40 | 9.31 | 8.20 | 11.56 | 14.03 |
| | $K_L$ /(L mg$^{-1}$) | 0.82 | 0.96 | 1.19 | 0.155 | 0.202 | 0.353 | 0.76 | 0.83 | 0.97 |
| | $R^2$ | 0.92 | 0.97 | 0.98 | 0.97 | 0.99 | 0.96 | 0.98 | 0.98 | 0.97 |
| | DAIC | 0.0 | | | 0.0 | | | 0.0 | | |
| Freundlich | $K_F^*$ | 5.19 | 5.94 | 7,52 | 1.77 | 2.06 | 2.89 | 3.20 | 4.72 | 5.94 |
| | $n$ | 0,22 | 0,24 | 0,22 | 0,39 | 0.37 | 0.33 | 0.27 | 0.31 | 0.33 |
| | $R^2$ | 0.76 | 0.86 | 0.88 | 0.90 | 0.93 | 0.87 | 0.90 | 0.89 | 0.84 |
| | DAIC | 39.3 | | | 41.4 | | | 47.4 | | |
| Tempkin | $B$ (mg g$^{-1}$) | 1.91 | 2.20 | 2.46 | 1.69 | 1.61 | 1.89 | 1.33 | 2.22 | 3,03 |
| | $K_T$ (L mg$^{-1}$) | 13.49 | 15.22 | 22.82 | 1.69 | 2.86 | 3.73 | 12.67 | 9.39 | 7.44 |
| | $R^2$ | 0.84 | 0.94 | 0.95 | 0.96 | 0.98 | 0.95 | 0.97 | 0.96 | 0.93 |
| | DAIC | 15.3 | | | 35.5 | | | 14.8 | | |

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 $R^2$. * units of $K_F$ (mg$^{1-(1/n)}$ L$^{1/n}$ g$^{-1}$)

The theoretical Langmuir equation (Langmuir, 1916) was originally applied to the adsorption of gases on a solid surface and, subsequently, to the liquid phase. The dynamic equilibrium of adsorption is related with the rate constants of adsorption and desorption. At equilibrium there is no net change, the sum of these two rates is zero, and the constant of this equilibrium (ratio between the adsorption and desorption rate constants) is the Langmuir equilibrium constant (KL). Assuming that, KL is essentially an equilibrium constant of the overall process that takes place during the phosphorus adsorption. So, its temperature dependence can be used to determine the isosteric enthalpy of adsorption, $\Delta_{ad}H^{o}$, using the Van't Hoff equation (Van't Hoff, 1887):

$$\left(\frac{\partial \, ln\, K}{\partial(1/T)}\right)_{\theta} = -\frac{\Delta_{ad}H^{\circ}}{R} \tag{5}$$

where *ln* denotes natural logarithm, *K* is the equilibrium constant, *T* is temperature, $\theta$ is the coating fraction, $\Delta adH^{o}$ is the enthalpy of adsorption and *R* the ideal gas constant.

Figure 34 shows the plot of the Van't Hoff equation of the experimental data. According to the eq. 5, the slope of each curve represents the isosteric enthalpy of adsorption for each adsorbent. The linearity of the curves is quite good, as shown by the high values of the coefficients of determination. The calculated values of the enthalpy are 13.38 kJ mol$^{-1}$, 8.49 kJ mol$^{-1}$ and 29.25 kJ mol$^{-1}$ for PWA, BSA and WSA adsorbents, respectively. These positive values indicate the endothermic nature of the global process that takes place during the phosphorus adsorption.

The reaction is endothermic. The adsorption capacity depends on the energy of the process. The greater the adsorption efficiency, the higher the temperature, which is what provides energy to the adsorption process.

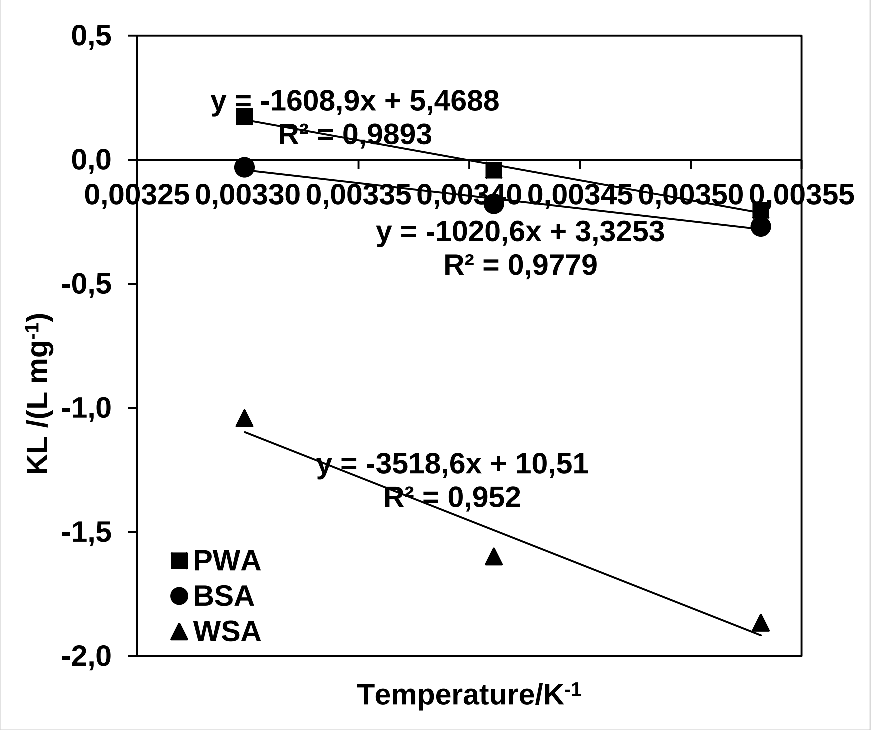

*Fig. 34: Thermodynamic plot for adsorption of phosphorus at 283, 293 and 303K.*

## 6.4. Conclusions

This study examined the adsorption of phosphorus by paulownia wood ash (PWA), burley straw ash (BSA) and wheat straw ash (WSA) under varying conditions. The results obtained have demonstrated the high capacity for phosphorus removal of the three tested ashes.

The dates obtained in characterization in the adsorbents indicate that the main elements are calcium and magnesium. On the other hand, the low percentage of carbon indicates that these materials are essentially inorganic.

Moreover, the results also demonstrated that the kinetic process lasted at least 96 h, and that the Langmuir adsorption model showed a better correlation with experimental equilibrium data.

The percentage of phosphorus removal varied significantly with the phosphorus-ash ratio: when the ash dose was increased, an increase in phosphorus removal was also observed.

With the PWA, the percentage of phosphorus removal varies (24.84–98.80%). With the WSA, the percentage of phosphorus removal varies (28.58–94.61%), and with the BSA, the percentage of phosphorus removal varies (42.29–98.49%).

Furthermore, increasing the temperature led to an increase of phosphorus removal and the positive values indicate the endothermic process.

So, PWA showed the best adsorption capacity of the three tested adsorbents, eliminating up to 12.01 mg $g^{-1}$ of phosphorus from synthetic wastewater with a concentration of 5 g $L^{-1}$ of adsorbent at 293 K in 96 h. BSA reached up to 11.96 mg $g^{-1}$ elimination of phosphorus with an adsorbent concentration of 5 g $L^{-1}$ at 293 K in the same period. WSA reached up to 8.39 mg $g^{-1}$ with an adsorbent concentration of 5 g $L^{-1}$ at 293 K.

Finally, the conducted research has demonstrated that after the production of energy in a biomass plant, the fly ashes of wood and/or straw can be reused to improve water quality by reducing the amount of phosphorus in contaminated water in rivers, lakes or lagoons, providing an environmentally sound low-cost remedial treatment.

Once the adsorption process is finished, the phosphorus-enriched ash waste generated could then finally act as a valorised fertilizer that farmers could reuse in their fields, fulfilling the objectives of the circular economy.

# 7. CONCLUSIONES

## 7.1 Principales conclusiones de la investigación

En esta tesis se avanza de forma significativa en el conocimiento científico sobre las capacidades de adsorción de contaminantes por cenizas de residuos vegetales con el fin de poder mejorar la calidad de las masas de agua en humedales protegidos que tienen aportaciones de aguas residuales, como es en el ejemplo del caso de estudio en el Parque Natural de L’Albufera de València. Esto se debe fundamentalmente a dos circunstancias, siendo la primera el conocimiento y, por lo tanto, la posibilidad de control de los procesos de adsorción de contaminantes mediante adsorbentes de bajo coste. Esta primera circunstancia genera la segunda, que es el interés científico que ha crecido considerablemente desde el año 2006, cuando empieza a aumentar la producción científica en relación con el estudio de los procesos de adsorción mediante residuos agrícolas como alternativa al uso masivo de fertilizantes minerales.

Así, tras la evaluación y discusión de todos los resultados obtenidos, se pueden extraer las siguientes conclusiones generales:

1) En primer lugar, se concluye que todas las cenizas tienen un carácter inorgánico debido a la baja concentración de carbono. Los compuestos químicos y elementos principales son óxidos de silicio, hierro, aluminio y cobre, además de estar formados por altas concentraciones de elementos alcalinos y alcalinotérreos, en su mayoría calcio y potasio. Físicamente, estos materiales son porosos debido a sus bajas áreas específicas y poseen una distribución heterogénea, no siendo en ningún caso cristalinos y poseyendo formas y tamaños diferentes.

2) En la fase experimental se determinaron y compararon las isotermas de Langmuir, Tempkin y Freundlich. De todas ellas se ha podido concluir que la isoterma que mejor ajuste posee al proceso de adsorción de fósforo mediante este tipo de materiales es la isoterma de Langmuir. Así, mediante esa isoterma se han podido estudiar y caracterizar las cinéticas de adsorción para cada tipo de ceniza de los materiales vegetales analizados. Estas cinéticas llegaron al equilibrio en caso de la ceniza de carrizo a los tres días, mientras que la ceniza de paja de arroz, ceniza de paja de arroz con tratamiento de HCl, ceniza de paja de cebada, ceniza de paja de trigo y ceniza de madera de paulownia llegaron al equilibrio cinético con un poco más de tiempo, concretamente a los 4 días. Además, estos materiales, una vez alcanzado el equilibrio, se mostraron constantes a lo largo del tiempo en semanas y meses.

3) En la investigación se han podido determinar las diferentes capacidades de eliminación de fósforo, que por lo general varían en sus porcentajes de eliminación entre un 20% y más de un 90%. Así, por orden creciente de sus máximos porcentajes de eliminación, la primera es la ceniza de paja de arroz con tratamiento de HCl (1M) que varía desde 17% hasta el 89%, para las cenizas de paja de arroz sin tratamiento de HCl (1M) varía desde el 32% hasta el 97%, para la ceniza de paja de trigo, varía desde el 29% hasta el 95%, para la ceniza de carrizo varía del 68% hasta el 98%, para la ceniza de paja de cebada varía desde el 42% hasta el 98%, y para las cenizas de madera de paulownia varía desde 25% hasta el 99%.

4. En cuanto a las capacidades de adsorción, también se ha podido determinar la relación entre la adsorción en mezclas de ceniza de paja de arroz sin tratamiento de HCl (1M) y ceniza de carrizo. Los resultados son positivos, ya que se determina una correlación lineal entre las mezclas realizadas con diferentes materiales y la capacidad de adsorción de éstos.

5. De los resultados obtenidos, también se ha podido concluir que la fuerza iónica ejercida por iones de sodio y cloruro tiene un ligero efecto positivo sobre la capacidad de adsorción de fósforo en la muestra de ceniza de paja de arroz sin tratamiento de HCL (1M) y carrizo, pero no presenta efecto alguno sobre la muestra de ceniza de paja de arroz con tratamiento de HCL (1M). También los estudios realizados muestran que una mayor concentración de metales alcalinotérreos (en este caso, calcio) implica mayor adsorción. Esto explica que la muestra tratada con HCL (1M) posea menor capacidad de adsorción, ya que el tratamiento reduce la cantidad de calcio y magnesio.

6. El efecto del pH se estudió para la ceniza de carrizo y para la ceniza de paja de arroz con y sin tratamiento de HCL (1M). Se ha podido establecer la relación entre pH inicial y pH final, pudiéndose observar que estas cenizas poseen un efecto tampón. En cuanto a la capacidad de adsorción se ha podido demostrar que la ceniza de paja de arroz sin tratamiento tiene mayor capacidad de adsorción de fósforo que la ceniza de paja de arroz con tratamiento con HCl (1M).

7. También se ha podido demostrar en la investigación que el efecto de la dosis del adsorbente varía la capacidad de adsorción a temperatura constante para todos los tipos de cenizas estudiados. También se puede concluir que al aumentar la dosis de adsorbente se reduce la capacidad de adsorción máxima de forma significativa, aunque, por la otra parte, aumenta la cantidad total de fósforo eliminado. En la fase experimental se determinó que el orden de capacidad de adsorción para las muestras estudiadas se mueve entre los 2,6 mg·g$^{-1}$ para ceniza de paja de arroz con tratamiento con HCl (1M) y los 29,3 mg·g$^{-1}$ para la ceniza de carrizo.
8. Los resultados de la investigación también demuestran que un aumento en la temperatura influye directamente en un aumento en la capacidad de adsorción para todas las cenizas de los materiales estudiados. Así, las entalpias de todas las cenizas son siempre positivas o endotérmicas cuando se produce el proceso de adsorción. Sin embargo, en la ceniza de carrizo se observa que al aumentar la temperatura de forma considerable (hasta 303 K) con altas concentraciones de fósforo, la reacción pasa de ser endotérmica o positiva a ser exotérmica o negativa, deteniéndose entonces el proceso de adsorción.

9. Como conclusión de toda la investigación, se puede afirmar que la ceniza de los diferentes materiales vegetales analizados, enriquecida por la adsorción de fósforo, puede ser utilizada como fertilizante natural. Por ello, se podrían revalorizar los residuos vegetales producidos en la zona de estudio, el Parque Natural de L’Albufera de València. Así, estos residuos podrían usarse para la depuración de las

aguas residuales que entran al lago mediante procesos de adsorción. Además, una vez finalizada la vida útil del adsorbente, junto al fósforo eliminado del agua residual, se podría utilizar como fertilizante natural para los cultivos de arroz como alternativa al uso actual de fertilizantes minerales, cerrando así el ciclo de una bioeconomía circular en el parque natural.

## 7.2 Caso hipotético de aplicación de resultados

En este apartado se explica un caso hipotético con los datos obtenidos en los diferentes experimentos de esta investigación y con datos de balsas ficticias.

Los datos experimentales son las capacidades de adsorción ($q_e$ en $mg \cdot gr^{-1}$), la concentración de fosforo total en el agua en $mg \cdot L^{-1}$, el tiempo que tarda en llegar la adsorción a equilibrio (días y/o horas), la relación de ceniza y agua en $g \cdot L^{-1}$ y la temperatura en grados Kelvin.

Los datos ficticios son el volumen de agua a tratar 20.000.000 L y el número de balsas a tratar.

Se pretende recuperar el fósforo de 6 balsas con un volumen de 20.000.000 L y una concentración de fósforo total de 15 $mg \cdot L^{-1}$ con una temperatura de 293K (20$^{o}$C).

Se disponen de ceniza de paja de arroz tratada con HCL, paja de arroz, paja de trigo, paja de cebada, de carrizo y de paulownia con capacidades de adsorción ($q_e$) de 1,260 $mg \cdot gr^{-1}$, 2.286 $mg \cdot gr^{-1}$, 2,805 $mg \cdot gr^{-1}$, 2.874 $mg \cdot gr^{-1}$, 2.886 $mg \cdot gr^{-1}$ y 2.918 $mg \cdot gr^{-1}$ respectivamente. Si se añaden estas cenizas al agua de la balsa con una relación de 5 $g \cdot L^{-1}$ (5 $kg \cdot m^{-3}$)

¿Qué cantidad de fósforo hay por balsa?

$$300\ kg\ fosforo = \frac{20.000.000L * 15\ mg\ L^{-1}}{1.000.000\ mg\ kg^{-1}}$$

¿Qué cantidad de ceniza se debe de aportar?

$$100\ t\ ceniza\ por\ balsa = \frac{20.000.000L * 5\ \ g\ L^{-1}}{1.000.000\ g\ tn^{-1}}$$

¿Qué cantidad de fósforo se puede recuperar?

Mediante la siguiente ecuación se pueden obtener las cantidades de fósforo recuperadas, para cada tipo de ceniza (o cada balsa).

$$kg\ fósforo\ total\ recuperado = \frac{g\ ceniza\ en\ balsa * q_e\ mg\ g^{-1}}{1.000.000\ g\ kg^{-1}}$$

Para la paja de arroz tratada con HCL, paja de arroz, paja de trigo, paja de cebada, de carrizo y de paulownia se recuperarían 126 kg de P, 228,6 kg de P, 280,5 kg de P, 287,4 kg de P, 288,6 kg de P y 291 kg de P respectivamente.

¿Qué porcentajes de fósforo se puede recuperar?

Para la paja de arroz tratada con HCL, paja de arroz, paja de trigo, paja de cebada, de carrizo y de paulownia se recuperarían el 42,0% de P, 76,2% de P, 93,5 de P, 95,8 de P, 96,2% de P y 97,3% de P respectivamente.

¿Qué concentración quedaría de fósforo sin adsorber en el agua?

Para la paja de arroz tratada con HCL, paja de arroz, paja de trigo, paja de cebada, de carrizo y de paulownia quedarían las concentraciones de 8,7 $mg{\cdot}L^{-1}$ de P, 3,57 $mg{\cdot}L^{-1}$ de P, 0,975 $mg{\cdot}L^{-1}$ de P, 0,63 $mg{\cdot}L^{-1}$ de P, 0,57 $mg{\cdot}L^{-1}$ de P y 0,45 $mg{\cdot}L^{-1}$ de P respectivamente.

¿Cuántos días tardaría en llegar a equilibrio la adsorción?

Llegaría al equilibrio a los 4 días (96 horas) para todas las cenizas excepto para el carrizo que llegaría a los 3 días (72 horas).

## 7.3 Futuras líneas de investigación

Tras los resultados obtenidos de toda la investigación en el marco de esta tesis doctoral y tras las conclusiones extraídas, se proponen las siguientes futuras líneas de investigación con el fin de poder avanzar en el conocimiento científico de la materia:

1. Una de las futuras líneas de investigación que surgen de esta tesis es el desarrollo y el estudio de procesos en continuo para analizar el comportamiento de los materiales que aquí se han estudiado solo en procesos discontinuos.

2. Otra línea que se propone es estudiar la capacidad de adsorción de otros productos o residuos generados en la zona de influencia en procesos productivos agrícolas, forestales o marinos como la *Posidonia oceanica,* como base para la mejora de la bioeconomía circular a nivel local.

3. Añadiendo a las anteriores líneas de investigación, otra línea es la determinación de la adsorción en materiales que no han sido incinerados previamente, como las diatomeas, que mediante diferentes procesos químicos (p.e. zeolitización de diatomeas) podrían aumentar su capacidad de adsorción.

4. Por último, también puede resultar de interés el estudio de materiales ricos en carbonato cálcico para la adsorción del fósforo, como pueden ser la piedra caliza, los residuos generados en el corte de mármoles o residuos ricos en cenizas, como los residuos de la construcción como el hormigón, teniendo en cuenta los tratamientos químicos previos necesarios y el estudio en detalle de todos los impactos que pueden generar.

# 8. TRANSFERENCIA DE LOS RESULTADOS DE LA INVESTIGACIÓN

## 8.1 Publicaciones científicas

Como principales resultados de transferencia del conocimiento adquirido en la presente Tesis Doctoral, cabe destacar que se han presentado tres artículos científicos que han sido publicados en tres revistas indexadas por el *Journal Citation Report* (JCR) durante el año 2020.

A continuación, se enumeran los artículos:

1) Carricondo, J.M., González, J.A., Mengual, J., Turégano, J.V., Oliver-Villanueva, J.V., (2020). Alternative use of rice straw ash as natural fertilizer to reduce phosphorus pollution in protected wetland ecosystems. *International Journal Recycling of Organic waste in Agriculture*. 9:61-74. https://doi.org/10.30486/IJROWA.2020.1885299.1003

2) Carricondo, J.M., Oliver-Villanueva, J.V., Turégano, J.V., González, J.A., Mengual, J., (2020). Use of *Phragmites australis* for controlling phosphorus contamination in anthropogenic wetland ecosystems. *Environmental Technology. (Online)* https://doi.org/10.1080/09593330.2020.1720311

3) Carricondo, J.M., Oliver-Villanueva, J.V., Turégano, J.V., Raigón, M.D., González, J.A., Mengual, J., (2020). Reduction of phosphorous from wastewater through adsorption processes reusing wood and straw ash produced in bioenergy facilities. *Water, Air & Pollution*. 231:128. https://doi.org/10.1007/s11270-020-04502-4

## 8.2 Participación en congresos, conferencias y seminarios científicos

En cuanto a la transferencia por congresos, conferencias y seminarios, hasta la fecha en que se presenta esta memoria, se ha participado en dos congresos mediante dos contribuciones publicadas en forma de póster en las actas del 16th *International Conference on Wetland for Water Pollution Control* de la *International Water Association* durante al año 2018.

1) Carricondo, J.M., González, J.A., Mengual, J., 2018. Water pollution control in a natural wetland using their own agro-waste, in: International Water Association. 16th IWA International Conference on Wetland Systems for Water Pollution Control, València, pp. 664–667.

2) Carricondo, J.M., González, J.A., Mengual, J., 2018. An alternative use of vegetation of treatment wetlands for the control of phosphorus contamination, in: International Water Association. 16th IWA International Conference on Wetland Systems for Water Pollution Control, València, pp. 668–671.

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# 10. ANEXOS: MATERIAL SUPLEMENTARIO

En este apartado se introduce los materiales suplementarios de los capítulos I, II y III.

## 10.1. Anexo 1.

El anexo 1 dispone del material suplementario del Capítulo I: "Alternativa al uso de paja de arroz como fertilizante natural reduciendo la contaminación de fósforo en humedales protegidos".

Aquí se muestran en la figura 35 diferentes imágenes de microscopia de barrido electrónico de la paja de arroz y de la figura 36 de paja de arroz sumergida en HCl (1M). Además, se describe el ajuste de la linealización de la isoterma de Langmuir.

### 10.1.1. Micrografía electrónica de barrido de adsorbentes

*Fig. 35: Scanning electron micrograph of RSA adsorbent.*

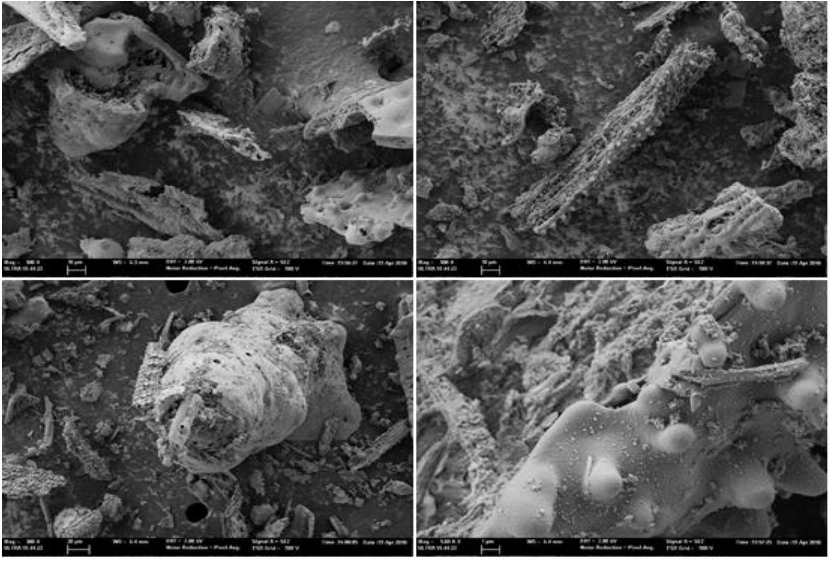
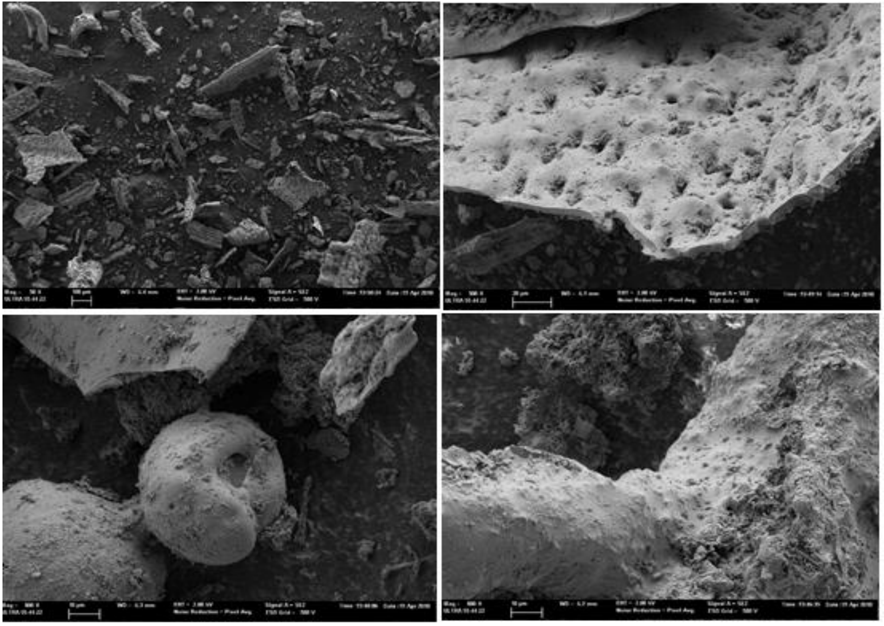


*Fig. 36: Scanning electron micrograph of RSA-H adsorbent.*



## 10.1.2. Ajuste de las diferentes linealizaciones de la isoterma de Langmuir

Non-linearized:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

Type I:

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

Type II:

$$\frac{q_e}{C_e} = -K_L q_e + q_{max} K_L$$

Type III:

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

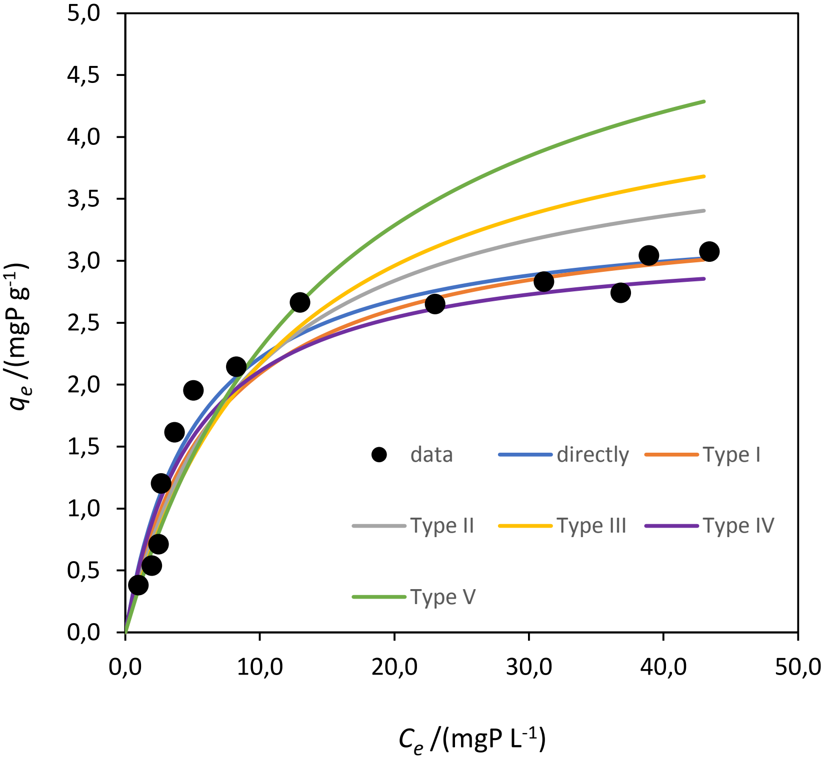
Type IV:

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

Type V:

$$\frac{1}{C_e} = K_L q_{max} \frac{1}{q_e} - K_L$$

*Fig. 37: Fit of the different linearization of the Langmuir isotherm over RSA at 283 K. Dose of adsorbent, 10 g L$^{-1}$.*



## 10.2. Anexo 2.

El anexo 2 dispone del material suplementario del Capítulo II: “Uso del carrizo (*Phragmatites australis*) para el control de la contaminación de fósforo en ecosistemas de humedales antropogénicos”

En este anexo se disponen de dos figuras, mostrando en la figura 38 el porcentaje de eliminación de fósforo con diferentes cantidades de ceniza de carrizo a temperatura constante; en la figura 39 muestra el porcentaje de eliminación de fósforo con misma cantidad de ceniza a diferente temperatura.

## 10.2.1. Porcentajes de eliminación de fosforo mediante ceniza de carrizo

*Fig. 38: % removal of reed ash in conical flask with 0.5,1.5,2.5 and 5 g L$^{-1}$ in reed ash and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 ppm of phosphorous, at 293K.*

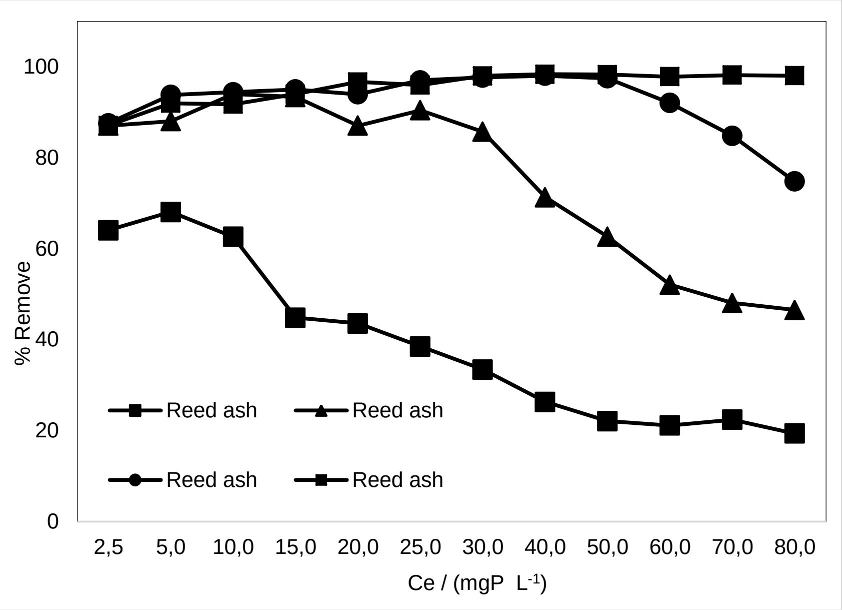
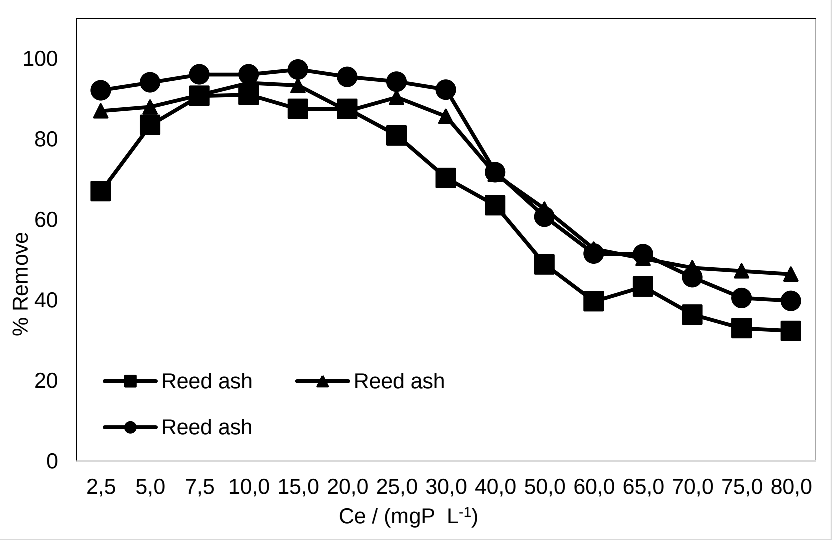


*Fig. 39: % removal of Reed ash in conical flask with 1.5 g L$^{-1}$ and 2.5, 5, 7.5,10, 15, 20, 25, 30, 40, 50, 60, 65, 70, 75, 80 ppm of phosphorous, at 283, 293 and 303 K.*



## 10.3. Anexo 3.

El anexo 3 dispone del material suplementario del Capítulo III: “Reducción de fósforo de aguas residuales a través de procesos de adsorción reutilizando cenizas de madera y paja producidas en instalaciones de bioenergía”.

En este anexo se disponen de dos figuras, mostrando en la figura 40 el porcentaje de eliminación de fósforo con diferentes cantidades de ceniza de paja de trigo, ceniza de paja de cebada y ceniza de madera de paulonia a misma temperatura y en la figura 41 se muestra el porcentaje de eliminación de fósforo con misma cantidad de ceniza a diferentes temperaturas.

### 10.3.1. Porcentajes de eliminación de fosforo mediante ceniza de paja de trigo, ceniza de paja de cebada y ceniza de madera de paulonia.

*Fig. 40: % removal of PWA, BSA and WSA in conical flask with 1.5, 2.5 and 5 g $L^{-1}$ for PWA and 2.5, 5, 10 g $L^{-1}$ for BSA and WSA with 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 mg $L^{-1}$ of phosphorus, at 293 K.*

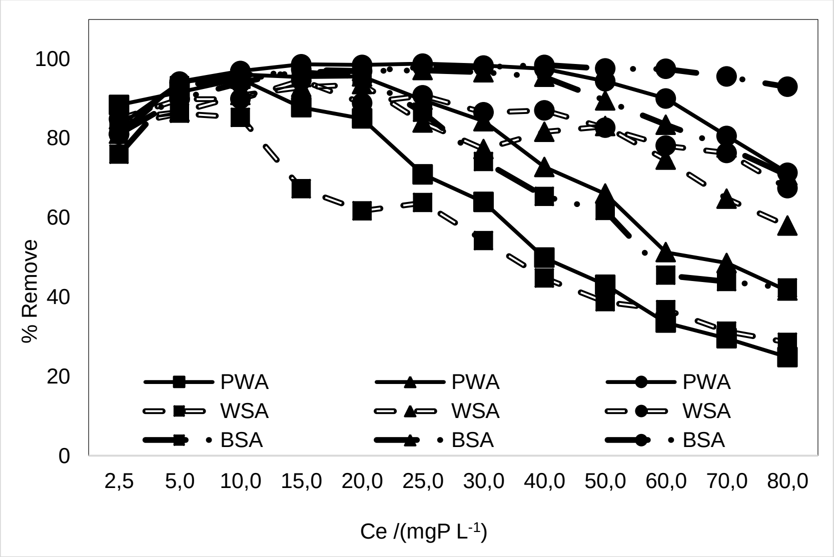


*Fig. 41: % removal of PWA, BSA and WSA in conical flask with 2.5 g L$^{-1}$ for PWA and 5 g L$^{-1}$ for WSA and BSA and 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 mg L$^{-1}$ of phosphorus, at 283, 293 and at 303 K.*