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Natural seagrass residues transformed into a phosphorous absorbing ally by becoming a fertilizer

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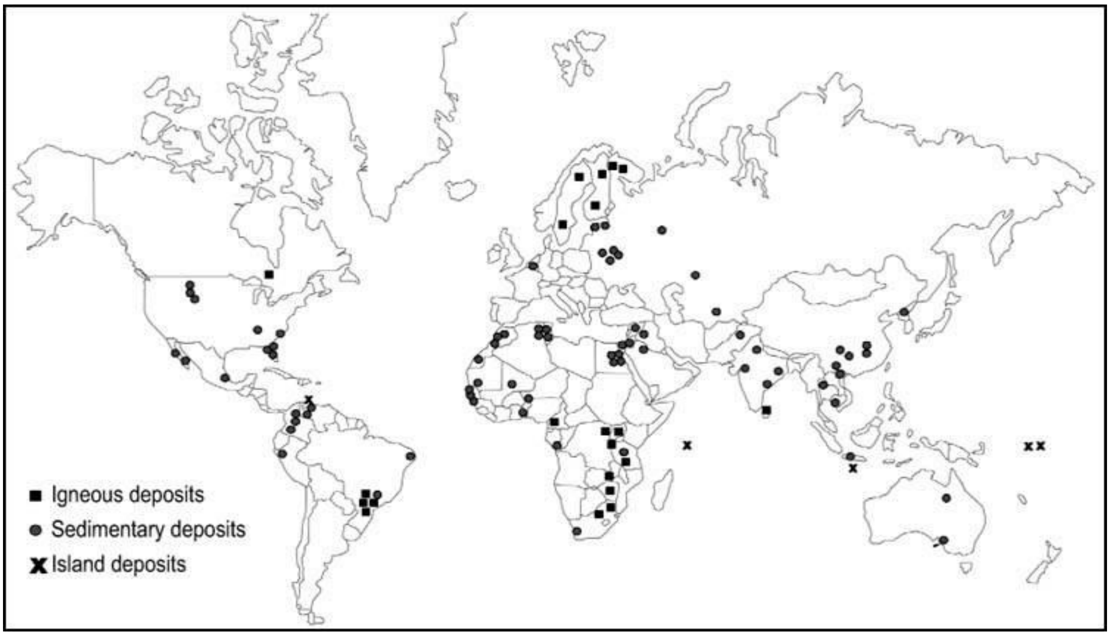
Abstract

This project aims to investigate the potential use of thermally treated seagrass *P. Oceanica* to recover phosphate from wastewater and the production of a fertilizer substitute. *Posidonia Oceanica* residues were thermally treated at 550^{o} C for 15 minutes and were tested as an adsorbent of phosphate for water collected from Finikaria dam. Results shows that thermally treated seagrass could be applied as adsorbents for Phosphate from synthetic and waster from dam (high in phosphorous), with 98% and 97% adsorption efficiency, respectively. Finally, by using thermally treated *P. Oceanica*, which was exposed to phosphate, as a potential fertilizer to lens it seems to positively affect their growth.

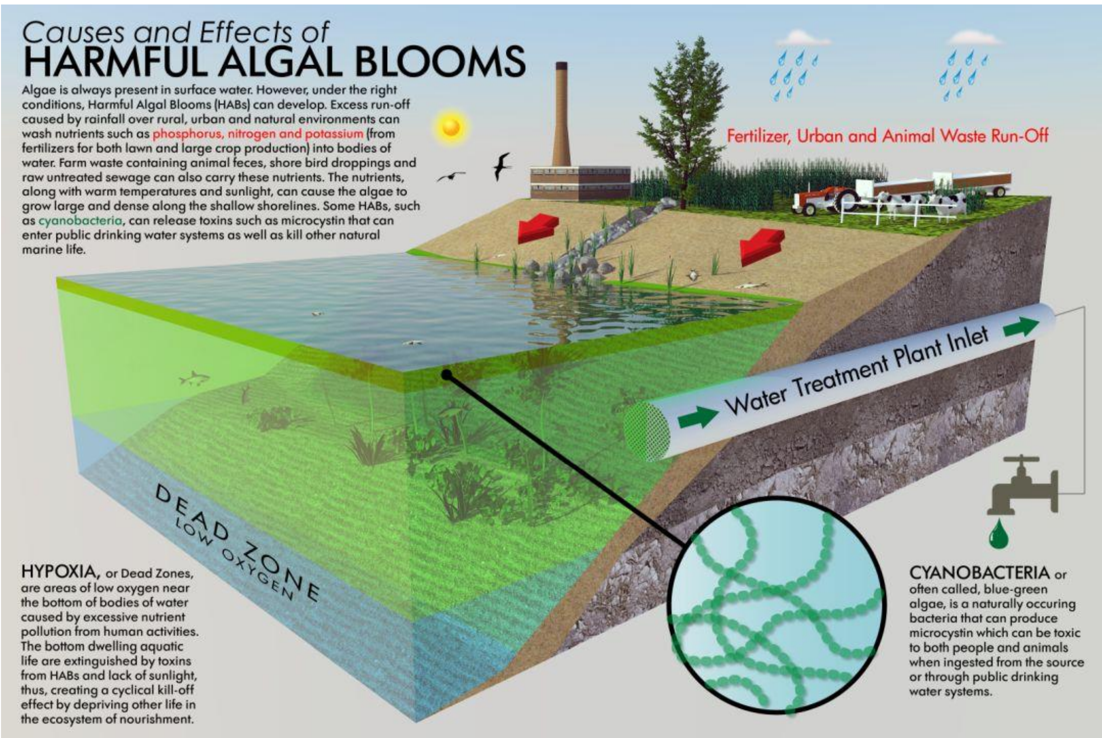
1 Literature Review

Phosphorus is an irreplaceable element for all organic lives, and phosphorus-based fertilizers are mainly produced from the mining of phosphate rocks. Phosphate rocks are gradually decreased, and they can be found only in certain countries (Picture 1), resulting in a strong import dependency and insecurity for the countries with a limited amount of phosphate rocks. (Cordell et al., 2009; Quist-Jensen et al., 2018; Monea et al., 2020). Scientists and engineers search for alternatives phosphorus sources and research directed towards efficient and sustainable processes for phosphorus recovery from those sources (Luyckx et al., 2020).



Picture 1: Phosphate deposits of the world
Source: The Food and Agriculture Organization of the United Nation (FAO)

Due to the wide use of phosphates in the industrial sector, it constitutes an important material for various industries that produce streams of wastes with high phosphorus content (Biswas et al., 2007). Nevertheless, excessive phosphorus concentration in water bodies is known to stimulate algal growth by reducing the dissolved oxygen in aqueous environment, which in turn, imposes a harmful effect on the aquatic life (Biswas et al., 2007). Moreover, high Phosphate (PO_4^{3-}) anions concentration can trigger algal growth (eutrophication), reducing the dissolved oxygen in aqueous environment, which not only kills the aquatic life by dropping the oxygen too low for the fish, but also disrupts the natural food chain (Ye et al., 2016).



Picture 2: Harmful algal blooms
Source: National Pond Service – Educational Resources

Eutrophication is the process of increase of plant nutrients in water with the consequent increase in the growth of algae and higher plants. This process is facilitated by external and internal (such as nitrogen fixation) sources of nutrients. Input of nutrients may be from point or diffuse sources. With phosphorus in particular, released from sediments can be a major source of this nutrient in water. In freshwater environments, anthropogenic inputs of nutrients (cultural eutrophication) have been demonstrated to be a major contributing factor to eutrophication and consequent algal blooms. In marine and estuarine systems, cultural eutrophication tends to enhance the input of nitrogen and phosphorus. This results in dominance by cyanobacteria and dinoflagellates. The formation of algal blooms in freshwater and marine ecosystems can result in the production of toxins depending on the species of algae present. A number of toxins can be produced that have ecological and human health impacts. Freshwater cyanobacteria produce hepatotoxins that can be present in drinking water. Marine dinoflagellates can produce various toxins including paralytic shellfish toxins, diarrheic shellfish toxins, amnesic shellfish toxins and ciguatoxins. In addition to toxin producing algae, a number of freshwater and marine species can be regarded as nuisance algae. These cause problems in water treatment and deleteriously affect the aesthetics of marine waters (Glendon et al., 2016).

As a result, Phosphorus recovery from water and wastewater has therefore recently become a topic of extreme scientific and technological interest. Various technologies are currently available for controlling phosphorus pollution. These processes can be classified as chemical (precipitation, crystallization, anion exchange, and adsorption), biological (assimilation, enhanced biological Phosphorus removal, constructed wetlands, wastewater stabilization pond), and physical (microfiltration, reverse osmosis, electrodialysis, magnetic separation). Among the numerous technologies adsorption offers various advantages, such as low cost, high efficiency and selectivity, simplicity in operation, and nondetectable influence on wastewater pH (Rathod et al., 2014).

Phosphorus recovery from wastewater has become an increasingly important area of research and technological development in recent years. One of the prominent technologies for phosphorus recovery is struvite precipitation. This process involves adding magnesium and ammonia to wastewater, creating struvite crystals that contain phosphorus. These crystals can then be separated and harvested, providing a valuable source of phosphorus for use in fertilizer production. Struvite precipitation not only helps in removing phosphorus from wastewater but also prevents its release into receiving water bodies, reducing the risk of eutrophication. Additionally, this technology offers the potential for cost-effective and sustainable phosphorus recovery, contributing to the circular economy and reducing dependence on finite phosphate rock reserves.

Another promising technology for phosphorus recovery is the use of algae-based systems, such as algae ponds or bioreactors. Algae have a natural ability to accumulate phosphorus from wastewater and can be harvested to extract this valuable nutrient. Algae-based systems offer several advantages, including their high phosphorus uptake efficiency, ability to grow in different wastewater conditions, and potential for simultaneous nutrient removal and biofuel production. Moreover, the harvested algae can be used as a nutrient-rich biofertilizer or processed into other valuable products. This technology not only helps in mitigating the environmental impact of wastewater discharge but also provides a sustainable approach to phosphorus recovery while harnessing the potential of microalgae for various applications.

Another approach to phosphorus recovery is enhanced biological phosphorus removal (EBPR), which allows for the simultaneous removal and recovery of phosphorus through biological processes. This technology reduces sludge production, integrates well with existing wastewater treatment systems, and offers the potential for energy recovery through anaerobic digestion of surplus biomass. However, achieving efficient phosphorus removal and recovery with EBPR requires well-controlled and optimized operating conditions. Sensitivity to influent variations and environmental conditions, as well as the potential for struvite formation, need to be carefully managed. Ion exchange is another technology that offers highly efficient phosphorus removal and selective recovery options. It enables targeted recovery but involves frequent resin regeneration, which increases chemical usage and operational costs. Moreover, the presence of competing ions in wastewater can reduce the effectiveness and lifespan of ion exchange resins, necessitating proper management

Previously, activated carbon or anion exchange resins have been used for Phosphorus decontamination. However, the problems associated with the high cost, no renewability, requirement of preconcentration of anions, and disposal after use hinder their widespread application in developing countries (Karthikeyan et al., 2004). Hence, increasing attention has been paid to waste-based products in an attempt to search for a viable alternative option that can be low cost, have high efficiency, good selectivity, potential renewability, and high adaptability to various process parameters (Jyothi et al., 2012). Adsorption constitutes the most favourable and well-established technique for pollutant removal and recovery due to the high affinity with nutrients and the low cost of sorbent materials (Humayro et al., 2021). In addition, using a modified biowaste as an adsorbent potentially offer a solution to two problems: biowaste management (P. oceanica residues) and phosphate recovery from wastewater.

Posidonia Oceanica is an endemic species in the Mediterranean Sea, and its dead leaves are accumulated in enormous quantities along sandy coasts, especially in autumn. *Posidonia Oceanica* is a key foundation species that provides habitat for a plethora of species including those of commercial interest and others that live exclusively in its meadows. In addition, P. oceanica meadows are important carbon dioxide sinks and sources of oxygen (Campagne et al., 2015), contribute to the protection of coastal environments against erosion by stabilizing soft bottoms and reducing the strength of currents and swell (Boudouresque et al., 2017;)

Nevertheless the excess dead leaves of P. oceanica cause aesthetic problems on the beach (Cengiz and Cavas, 2010), and its treatment collection and transportation has a high cost (Photiou et al., (2021). The dead leaves of *P. Oceanica* are very promising biomass source for adsorption (Photiou et al.,2021). Specifically, the applicability of treated *P. Oceanica* residues in the adsorption process has been reported in several studies in the literature for the removal of orthophosphates, textile dyes (Guezguez and Mhenni, 2008), methylene blue (Dural et al., 2011), anionic and non-ionic surfactants (Ncibi, 2008), phenol (Ncibi et al., 2014) and heavy metals (Asimakopoulos et al., 2021).

This study's main purpose was to examine the phosphate adsorption from Finikaria dam using a modified biowaste (P. Oceanica residues) and produce a product after adsorption that can be used through its direct application as a soil supplement. The research took place between October 2022 and February 2023 by high school students in Limassol, Cyprus under surveillance of the Cyprus University of Technology Assistant Professor Ioannis Vyrides and Associate Professor Georgios Constantinides.

1.1 Problem identification

Phosphorus is a key component of municipal waste - by virtue of its existence of in various daily products – and the amounts of phosphorus in aquatic receptors are a significant problem as they cause eutrophication and the loss of aquatic organisms and plants due to lack of oxygen and obstruction of solar radiation. Efforts are being made to prevent harmful environmental from excess phosphorus and various techniques have been devised to remove phosphorus. Until recently the most common way to remove phosphorus was chemical precipitation using calcium clay or iron salts. Most of these techniques require a long period of time and great financial costs for the application of phosphorus removal. Furthermore, with these methods only 30% of phosphorus can be removed.

There is a wide variety of materials that can be used as adsorbents for phosphorus from waste and much more economically thereby achieving the creation of greener materials and technologies. Such material is excess dead leaves of *P. oceanica*. Moreover, the excess dead leaves of *P. oceanica* cause aesthetic problems for Cypriot beaches since such an image deters tourists and creates a problem for Cyprus tourism. Due to this phenomenon local municipalities spend a lot of money for their removal and disposal to landfill.

Taking into consideration the above issues we designed the following experimental procedure aiming to address the following questions:

1. Can the excess dead leaves of *P. oceanica* adsorb phosphorus?
2. Can we use the dead leaves of *P. oceanica* to adsorb phosphorus and use it as a fertiliser?

2 Experimental Investigation and Results

2.1 Preparation of adsorption material seagrasses P. Oceanica

The dead leaves of *P. oceanica* are a promising material for the removal of phosphorus. Seagrasses can be found in many beaches in Cyprus and causes an aesthetic problem for tourists, us a result the Municipalities of the cities must pay a lot of money for their removal (Picture 3). For that reason, dead leaves of *P. Oceanica* are ideal, not only because many beaches exist in Cyprus so large amounts (70 – 80 tones) of dead seagrasses can be easily accessible, but also to reinforce the principles of 'circular economy'. The foundation of 'circular economy' in the idea that resources can be kept in use for as long as possible, then recover and regenerate products and materials at the end of each service life. This idea has been of particular interest in the European Union in the last few years, with the publication of a new policy entitled Circular Economy Closing the Loop (European Commission, 2015).

For our experiments dead leaves of *P. Oceanica* were collected from Limassol district (Karnagio area). Following the protocol at first, they were dried at room temperature for 48 h (Picture 5). Then we cut them into small pieces (Picture 6) and heated them in an oven (Picture 4) at 550^{o} C for 15 minutes. According to Photiou et al (2020), the optimal absorption of phosphate can be achieved when seagrass is heated 550^{o} C for the period of 15 minutes. Next, the seagrass residue was ground, and the powders produced were screened through a sieve lower than one millimetre (Picture 7).

Pictures 3: Dead leaves of *P. oceanica* from Limassol District (Karnagio Area)

Picture 4:
Oven for heating seagrass

Picture 5:
Dead leaves of P. *Oceanica* - *Seagrass*

Picture 6:
Seagrass cut in small pieces.

Picture 7:
Seagrass powder

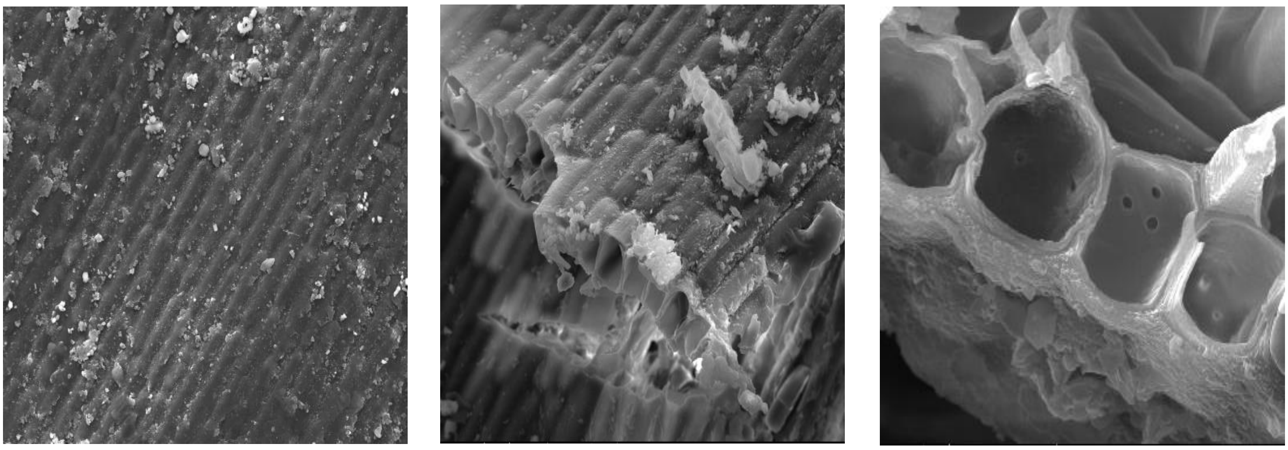
After heat treatment, part of the lining is decomposed exposing a higher surface area and the internal structure of the biomass which has also generated porous at the nanometre scale. Cubic structures pertaining to salt crystals are also visible both the received and treated materials. The salt resides primarily within the tubes and is exposed after heat treatment. By heating the seagrass and making it into powders we increase the surface area of the adsorbent and making it more effective.

A Scanning Electron Microscope (SEM) from FEI (Quanta 200) (Picture 8) has been used to acquire images of the surface topography of seagrass samples before and after heat treatment and phosphorous adsorption process. All samples were coated, prior to examination, with a thin (<10nm) silver layer (Picture 10) in order to increase surface conductivity and reduce electron charging from the microscope. Images were collected at 20kV accelerating voltage in various magnifications. Energy-dispersive X-ray spectroscopy (EDS) was also conducted along with imaging, to acquire information about the elemental composition of the samples. Elemental maps were also obtained to reveal spatial information about the phosphorous adsorption sites.

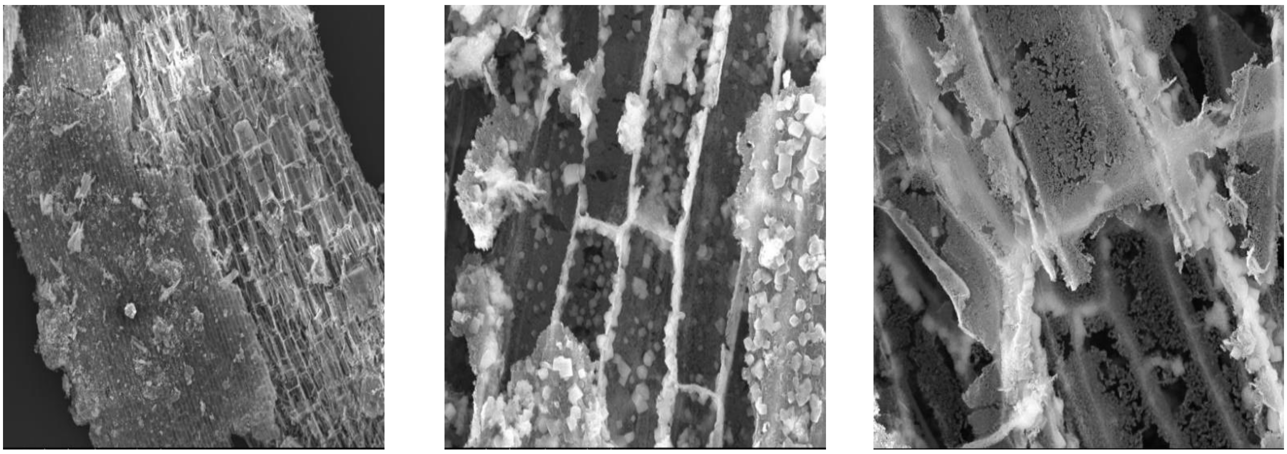
Picture 8:
Scanning Electron Microscope

Picture 9:
Seagrass powder

Picture 10:
samples with a thin silver layer



Picture 11: Seagrass powder using scanning electron microscopy.



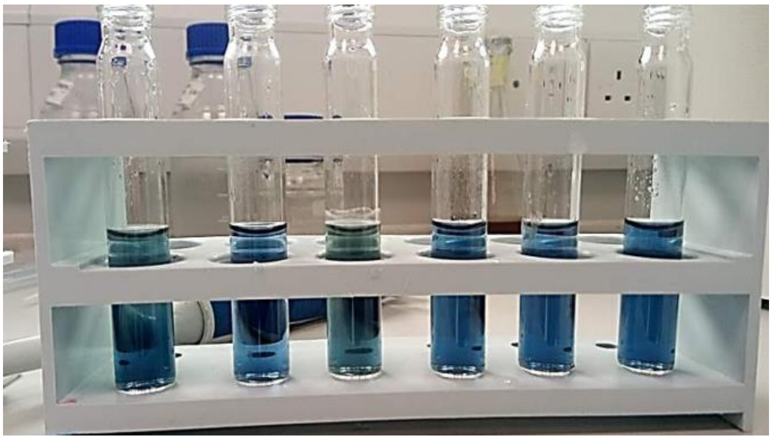
Picture 12: Thermally treated seagrass powder using scanning electron microscopy.

Comparing pictures 11 and 12 we can see that the heated seagrass has an increased number of porous than the non-heated seagrass, therefore more surface area which will conclude in more phosphate adsorption.

2.2 Preparation of experiment and samples

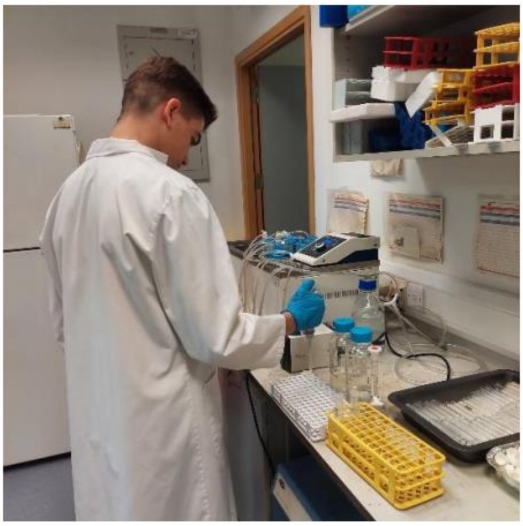
2.2.1 Synthetic sources of phosphate

According to United States Environmental Protection Agency municipal wastewaters may contain from 5 to 20 mg/L of total phosphorous, of which 1-5 mg/l is organic and the rest in inorganic. Synthetic solutions, containing the bibliography concentration, were prepared by dissolving anhydrous potassium dihydrogen phosphate (KH_2PO_4) with deionized water. The first bottle was used as control, including only 50 mg/L of phosphorus without any thermally treated seagrass in order not to have any adsorption. In the remaining bottles, we tested 50 mg/L synthetic solution exposed to 1g/L of thermally treated seagrass. The thermally treated seagrass were in contact with each solution for different period time so that we could test the adsorption capacity of the seagrass accounting to time of contact. The darker blue is the colour of dilution solutions the greater the amount of phosphorus in the samples (Picture 13).



Picture 13: Bottles with phosphorous synthetic solutions.

From the data obtained, the adsorption capacity was expressed as the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent. More specifically using UV/VIS spectrophotometer (JENWAY 7315, Staffordshire, UK) (Picture 15) at 880 nm, samples were subsequently withdrawn at regular intervals to monitor the adsorption process and phosphate was determined by the ascorbic acid method (Figure 1).



Picture 14:
Collecting samples

Picture 15:
Spectrophotometer JENWAY 7315

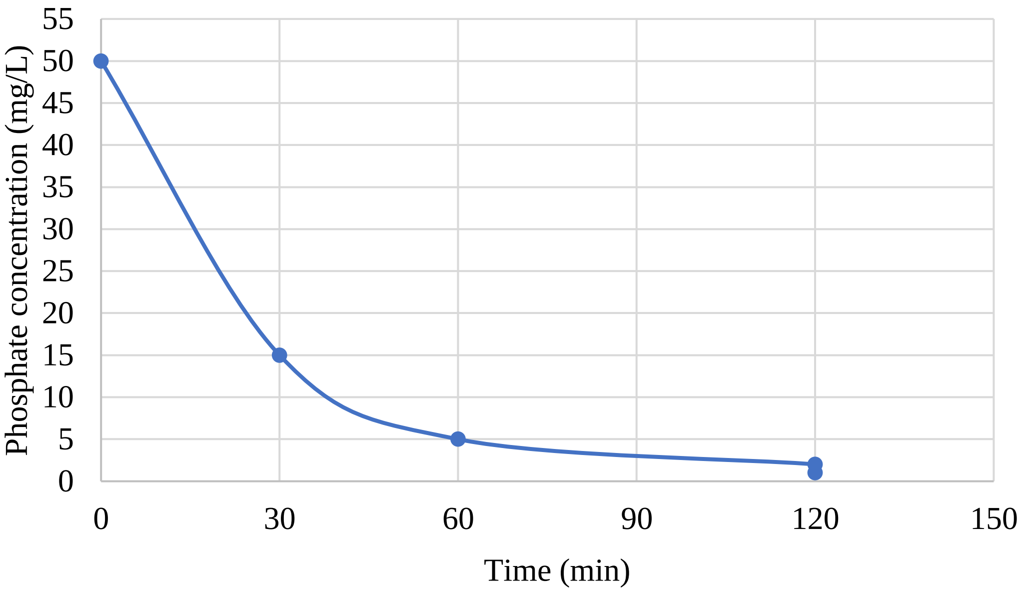


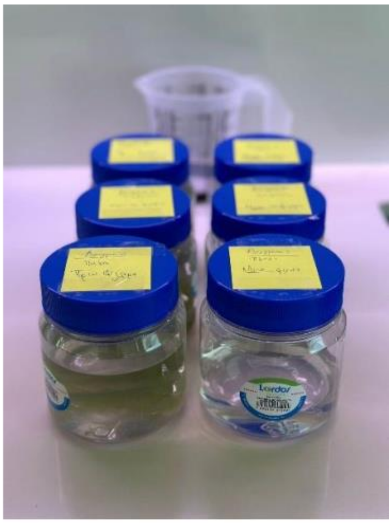
Figure 1: Concentration of phosphate over time from synthetic solution when exposed to thermally treated seagrass *P. Oceanica*

By observing the results, it is obvious that the concentration of phosphate concentration was reduced when exposed to with residual thermally treated seagrass P. *Oceanica*. In the first 30 min the results indicate that 70% of the initial phosphate concentration was adsorbed and by the end of the adsorption process the concentration of phosphate was reduced by 98%. This experiment shows the high capability of residual thermally treated seagrass to adsorption of phosphate in a relatively short time.

2.2.2 Real sources of phosphate

As real phosphate sources, water used in this study was collected from the Finikaria dam. Samples were collected in three bottles of 0,5 L capacity, one bottle includes sample from the surface (0 cm), the second includes sample from a depth of 50cm and the third bottle includes sample from a depth of 100 cm. Six samples were collected in total from Finikaria dam in November 2022 (Picture 16).





Picture 16: Samples from Finikaria dam

Then we made our own filter. We took a plastic bottle and closed it with a cotton cloth (Picture 17). First, we filtered through 50ml from our samples from the surface (0 cm) from Finikaria dam to examine if the cotton cloth would absorb any phosphorus. Then we placed the thermally treated seagrass in the filter and filtered through 50ml from our samples from Finikaria dam from the surface (0 cm), from a depth of 50cm and from a depth of 100 cm. For control we used the samples from Finikaria dam from surface (0 cm), from a depth of 50cm and from a depth of 100 cm without any treatment. Using UV/VIS spectrophotometer (JENWAY 7315, Staffordshire, UK) at 880 nm, samples were tested for adsorption of phosphate (Table 1).

Picture 17: Our filter

Water depth	**Concentration of phosphate in real water before filter***	**Concentration of phosphate in real water after filter***
0 cm (surface) Control	30 mg/L	25 mg/L
0 cm (surface)	30 mg/L	1 mg/L
50 cm	3 mg/L	1 mg/L
100 cm	3 mg/L	1 mg/L

Table 1: Samples from Finikaria dam,

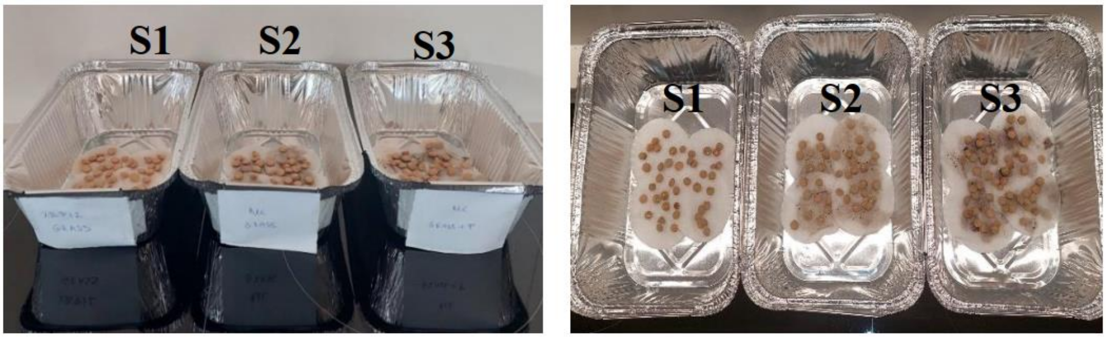
*Filter consisted of thermally treated seagrass *P. Oceanica*

By studying the results regarding the surface samples (0 cm), it is evident that, although the samples were filtered only once, the concentration of phosphate is reducing 97% when in contact with residual thermally treated seagrass *P. oceanica*.

It is also important to notice that when the surface sample 0 cm passed through the fabric, without the seagrass, there was a decrease in the concentration of phosphate. This may be since this sample also had residues particles which seem to have been retained by the fabric. However, having filtered through seagrass further reduced the concentration of phosphate. This may be since on the surface there are cyanobacteria and algae that accumulate the phosphorus inside them. Another important observation is that in the samples collected from depth of 50 cm and 100 cm had low concentration of phosphorus from the beginning.

2.3 Testing seagrass as fertilizer.

To examine if the seagrass P Oceania that has absorbed phosphorus can be used as a fertilizer, we conducted the following experiment. We placed the same amount of lentils onto wet cottons in three separate containers. In the first container (**S1) the lentils were watered with just drinking water**. In the second container (**S2) the lentils were watered with water which contained powdered thermally treated seagrass P. Oceanica without phosphorus**. In the third container **(S3) the lentils were watered with water that contained thermally treated seagrass P. Oceanica after the absorption of phosphorus**. The aim of this experiment is to observe the growth of the lentils on each occasion and to examine if seagrass P. Oceania can be used as a fertilizer after the absorption of phosphorus. All the lentils, despite being placed in different containers, were treated with the same care. Every day they were watered the same amount of water and they were placed sin the same room with the same sunlight and temperature for thirty days.

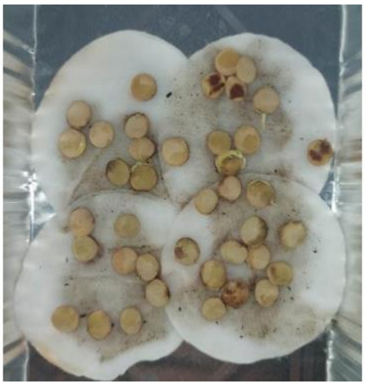


Day 1 (15/02/23)

S1 **S2** **S3**

Day 3 (14/02/23)


S1


S2


S3

Day 5 (19/02/23)


S1


S2


S3

Day 7 (21/02/23)


S1


S2


S3

Day 9 (23/02/23)

S1 **S2** **S3**

Day 13 (27/02/23)

S1 **S2** **S3**

Day 15 (01/03/23)

Day 13 (02/03/23)

We noticed that there was a difference in the growth of each container. The lentils that were watered with drinking water and the lentils that were watered with water that included thermally treated seagrass but without phosphorus had a slow growth compared to the lentils that were watered with thermally treated seagrass and phosphorus that had the fastest growth out of all groups, not only more lentils grew but also the size of the plants was bigger.

In general, the group of lentils that were watered with just water 7 out 42 lentils germinated. From the group that were watered with water that contained seagrass 9 out of 42 lentils germinated and lastly, from the group of lentils that were watered with water that contained seagrass which had previously absorbed phosphorus 16 out of 42 lentils germinated. That was an integration that thermally treated seagrass and phosphorus could be used as fertilizer.

The experiment with the lentils was only the first step, an easy way for us to test and find out whether the thermally processed seagrass that had already absorbed phosphorous could be used as a fertiliser.

The next step is for us to test the processed seagrass on several types of waste water and find out in which of the waste we would achieve the ideal absorption and hence removal of phosphorous. Moreover we would test that the final product that the deserved qualities to be successful used in a broaden aspect.

Discussion

The recovery of phosphorus from waste is of utmost importance as the increased levels of its concentrations contribute to the creation of undesirable eutrophication and not the simple growth of plants and other organisms. Therefore, it becomes necessary to treat the waste before their final disposal to the water receivers so that there is removal of dissolved phosphorus and its subsequent recovery for contribution in sustainable development.

During our research we used thermally treated seagrass *P. Oceanica* to recover phosphate from wastewater and the production of a fertilizer substitute. Assessment of the saturation capacity of thermally treated P. Oceanica confirmed the high capacity and selectivity towards phosphate. Adsorption experiments showed that thermally treated seagrass could be applied as adsorbents for Phosphate from synthetic and real wastewater solutions, with 98% and 97% adsorption efficiency, respectively. Then by using thermally treated *P. Oceanica*, which was exposed to phosphate, as a potential fertilizer to lens it seems to positively affect lens growth.

In conclusion, thermally treated seagrass residues showed high selective adsorption towards phosphate from real waster high in phosphorous. After adsorption, the solid residues were used as a fertilizer and pointed out a positive effect on plant growth. Overall, the proposed solution solves three problems: a) it can efficiently valorise seagrass residues instead of being transported to landfills, b) it can be a solution to counteract eutrophication in dams or lakes since the thermally treated seagrass has a high adsorption capacity through phosphate c) after adsorption the solid residue (thermally treated seagrass with phosphate) indicates that can be used as a fertilizer.

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