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**TECHNO-ECONOMIC EVALUATION OF ION EXCHANGE
TECHNOLOGIES TO RECOVER NITROGEN AND
PHOSPHORUS FROM MUNICIPAL WASTEWATER**



Report and Annexes

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Abstract

In the context of the circular economy, wastewater treatment plants (WWTPs) are undergoing significant transformations for the recovery of valuable resources. Among these resources, nitrogen and phosphorus are of particular interest to be valorised as fertilisers. Ion exchange processes, using selective resins capable of retaining these compounds, are presented as a promising alternative for the efficient recovery of nitrogen and phosphorus from wastewater. However, it is crucial to understand how the application of this technology can affect the economic balance of nutrient recovery/removal in a WWTP.

The objective of this project is to evaluate the economic feasibility of the application of ion exchange technologies for the recovery of nitrogen and phosphorus from municipal wastewater. It is proposed to treat a of 20,000 m³ of wastewater per day with a concentration of 56 mg L⁻¹ of NH₄-N and 14 mg L⁻¹ of PO₄-P. Pre-design and mass/energy balances will be carried out to evaluate the proposed alternatives and to obtain the necessary data for the economic evaluation. Sensitivity analyses of the most relevant design and economic parameters will also be carried out to identify the key factors affecting the economic viability of the process.

After a literature search on the most important components of the system, "Mesolite" zeolite has been selected as the ion exchange sorbent for nitrogen recovery, while a hybrid ion exchange resin (HAIX) with ferric oxide nanoparticles embedded in its structure will be used for phosphorus recovery. Subsequently, membrane technology with liquid-liquid membrane contactor (LLMC) will be applied to recover nitrogen in the form of ammonium sulphate, and crystallisation technology to recover phosphorus in the form of hydroxyapatite.

After assessing the economic viability of the system, the total net cost of the project has been determined to be approximately 80 million euros after 20 years of plant life. Although the cost of the project raises questions in financial terms, its value lies in the environmental and sustainable aspects, such as conservation of natural resources and compliance with environmental regulations.

In conclusion, this study confirms the feasibility of implementing ion exchange technologies in wastewater treatment and nutrient recovery, with potential to move towards a circular economy and sustainable water treatment.

Resum

Dins el context de l'economia circular, les estacions depuradores d'aigües residuals (EDAR) estan experimentant transformacions importants per a la recuperació de recursos valuosos. Entre aquests recursos, destaquen el nitrogen i el fòsfor com a fertilitzants de valor afegit. Els processos d'intercanvi iònic, utilitzant resines selectives capaces de retenir aquests compostos, es presenten com una alternativa prometedora per a la recuperació eficient de nitrogen i fòsfor de les aigües residuals. Tot i això, és crucial entendre com l'aplicació d'aquesta tecnologia pot afectar el balanç econòmic de la recuperació/eliminació de nutrients en una EDAR.

L'objectiu d'aquest projecte és avaluar la viabilitat econòmica de l'aplicació de tecnologies d'intercanvi iònic per a la recuperació de nitrogen i fòsfor de les aigües residuals municipals. Es proposa tractar un cabal diari de 20.000 m³ d'aigües residuals amb una concentració de 56 mg L⁻¹ de NH₄-N i 14 mg L⁻¹ de PO₄-P. Es realitzaran balanços de predisseny i massa/energia per avaluar les alternatives proposades i obtenir les dades necessàries per a l'avaluació econòmica. També es duran a terme anàlisis de sensibilitat dels paràmetres de disseny i econòmics més rellevants per identificar els factors clau que afecten la viabilitat econòmica del procés.

Després d'una cerca bibliogràfica sobre els components més importants del sistema, s'ha seleccionat la zeolita "Mesolite" com a mitjà d'intercanvi iònic per a la recuperació de nitrogen, mentre que per a la recuperació de fòsfor es farà servir una resina híbrida d'intercanvi iònic (HAIX) amb nanopartícules d'òxid fèrric incrustades a la seva estructura. Posteriorment, s'aplicarà la tecnologia de membranes (LLMC) per recuperar el nitrogen en forma de sulfat d'amoni, i la tecnologia de cristallització per recuperar el fòsfor en forma d'hidroxiapatita.

Després d'avaluar la viabilitat econòmica del sistema, s'ha determinat que el cost net total del projecte és d'aproximadament 80 milions d'euros després de 20 anys de vida útil. Tot i que el cost del projecte planteja interrogants en termes econòmics, el seu valor rau en els aspectes ambientals i sostenibles, com la conservació dels recursos naturals i el compliment de la normativa ambiental.

En conclusió, aquest estudi confirma la viabilitat d'implementar tecnologies d'intercanvi iònic en el tractament d'aigües residuals i la recuperació de nutrients, amb potencial per avançar cap a una economia circular i un tractament sostenible de l'aigua.

Resumen

En el contexto de la economía circular, las estaciones depuradoras de aguas residuales (EDAR) están experimentando importantes transformaciones para la recuperación de recursos valiosos. Entre estos recursos, destacan el nitrógeno y el fósforo como fertilizantes de valor añadido. Los procesos de intercambio iónico, utilizando resinas selectivas capaces de retener estos compuestos, se presentan como una alternativa prometedora para la recuperación eficiente de nitrógeno y fósforo de las aguas residuales. Sin embargo, es crucial entender cómo la aplicación de esta tecnología puede afectar al balance económico de la recuperación/eliminación de nutrientes en una EDAR.

El objetivo de este proyecto es evaluar la viabilidad económica de la aplicación de tecnologías de intercambio iónico para la recuperación de nitrógeno y fósforo de las aguas residuales municipales. Se propone tratar un caudal diario de 20.000 m³ de aguas residuales con una concentración de 56 mg L⁻¹ de NH₄-N y 14 mg L⁻¹ de PO₄-P. Se realizarán balances de prediseño y de masa/energía para evaluar las alternativas propuestas y obtener los datos necesarios para la evaluación económica. También se llevarán a cabo análisis de sensibilidad de los parámetros de diseño y económicos más relevantes para identificar los factores clave que afectan a la viabilidad económica del proceso.

Tras una búsqueda bibliográfica sobre los componentes más importantes del sistema, se ha seleccionado la zeolita "Mesolita" como medio de intercambio iónico para la recuperación de nitrógeno, mientras que para la recuperación de fósforo se utilizará un adsorbente híbrido (HAIX) con nanopartículas de óxido férrico impregnadas en su estructura polimérica. Posteriormente, se aplicará la tecnología de membranas (LLMC) para recuperar el nitrógeno en forma de sulfato de amonio, y la tecnología de cristalización para recuperar el fósforo en forma de hidroxapatita.

Tras evaluar la viabilidad económica del sistema, se ha determinado que el coste neto total del proyecto asciende aproximadamente a 80 millones de euros tras 20 años de vida útil de la planta. Aunque el coste del proyecto plantea dudas en términos financieros, su valor reside en los aspectos medioambientales y sostenibles, como la conservación de los recursos naturales y el cumplimiento de la normativa medioambiental.

En conclusión, este estudio confirma la viabilidad de aplicar tecnologías de intercambio iónico en el tratamiento de aguas residuales y la recuperación de nutrientes, con potencial para avanzar hacia una economía circular y un tratamiento sostenible del agua.





Acronyms

AnMBR	Anaerobic Membrane Bioreactor
BV	Bed Volume
CAPEX	Capital Expenditure
CAS	Conventional Activated Sludge
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred-Tank Reactor
EBCT	Empty Bed Contact Time
HAIX	Hybrid Anion Exchange Resin
IEX	Ion Exchange
LLMC	Liquid–liquid Membrane Contactor
N	Nitrogen
OPEX	Operational Expenditures
P	Phosphorus
PV	Present Value

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1. Introduction

Nitrogen (N) and phosphorus (P) are nutrients naturally present in aquatic ecosystems. Both elements are essential for all forms of life on aquatic environment as they support the growth of algae and aquatic plants, promoting the proliferation of fish, molluscs and small organisms living in the water. However, excess of nutrients can cause plants and other organisms to grow in abundance, leading to eutrophication, which consists in the depletion of large amounts of oxygen with a direct impact on the aquatic environment and human health (Huang et al., 2020). To prevent this problem, discharge limits for nitrogen and phosphorus from municipal wastewater have been established and are regulated by European and Spanish legislation. According to Directive 91/271/EEC concerning urban wastewater treatment, the emission limits for nitrogen and phosphorus in urban wastewater in sensitive areas in Spain are 2 mg L⁻¹ P and 15 mg L⁻¹ N for 10000 to 100000 PE, respectively, and 1 mg L⁻¹ P and 10 mg L⁻¹ N for values higher than 100000 PE, respectively (Directive 1991).

Phosphorus is a non-renewable resource that is mainly extracted from phosphate rock deposits, which are found in some regions of the world, such as Morocco, China, USA, and Russia. Due to the growing demand for food and agricultural products, the demand for phosphorus has increased significantly in recent decades (Cordell et al., 2009). This concentration of phosphate resources in some regions of the world makes their supply vulnerable to disruptions and large price fluctuations. In addition, phosphate mining can have serious environmental impacts, such as greenhouse gas emissions and water pollution. Some studies claim that phosphate reserves could be depleted in the next 50-100 years, while the costs of mining, processing and transport are expected to rise in the future (Smil, 2000; Mew et al., 2016).

On the other hand, nitrogen is a key element necessary for the growth and survival of living organisms. However, despite being one of the most abundant elements in the atmosphere, it is not available in a usable form for most organisms. The availability of N for use in agriculture and human food is crucial, which is why the production of nitrogen fertilisers has increased food production and improved crop quality, contributing to global food security (Tilman et al., 2002). However, nitrogen fertiliser production through the conventional Haber-Bosch process has negative environmental impacts as it is an energy-intensive process that emits large amounts of greenhouse gases (Motavalli et al., 2008). Furthermore, a study on the nitrogen cycle and its environmental impact (Galloway et al., 2013) concluded that most of the N produced by humans is lost to the environment, resulting in a cascade of negative impacts (acid rain, smog, eutrophication, greenhouse effect, etc). According to the authors, water and air pollution caused by nitrogen production and use is one of the greatest environmental challenges facing the world today.

As previously mentioned, N and P are valuable resources that need to be properly managed to avoid environmental problems. For this reason, the circular economy has emerged as a key strategy to address this problem based on the idea of closing material and energy cycles to minimise waste and maximise the value of resources. In particular, the recovery of nutrients from wastewater can avoid the problems related to the production and extraction of N and P from non-renewable sources, which represents a significant environmental burden in terms of greenhouse gas emissions and other environmental impacts. In addition, closing the nutrient cycle significantly improves water quality and can generate economic incomes through the sale of recovered fertilisers and other value-added products (Tarpeh et al., 2018).

Among the available technologies for nutrient recovery, ion exchange is a promising alternative as the resins can be selective in capturing ammonium and phosphate ions present in wastewater (Guida et al., 2021). Currently, several studies have evaluated the efficacy and feasibility of ion exchange technologies. For example, Johir et al. (2011) evaluated the removal and recovery of nutrients by ion exchange from high-rate membrane bioreactor (MBR) effluent, where the ion exchange process retained phosphate and ammonium by 85% and 95%, respectively.

However, large-scale implementation of this technology faces several technological and economic challenges. From the technological point of view, the main challenge relies on the ability to adapt to variations in wastewater characteristics as the presence of other compounds may reduce the efficiency of the process (Jorgensen & Weatherley, 2006). Another major challenge is related to the handling and disposal of the waste generated in the ion exchange process as the resins may require high concentrations of chemicals in the regeneration stage, which increases the cost and complexity of the process. From an economic point of view, the main challenge is to reduce the capital and operating costs of ion exchange technologies. In addition, optimisation, and integration of the ion exchange process with other wastewater treatment processes is a key parameter to reduce costs (Canellas-Garriga, 2018).

In summary, the recovery of nutrients from wastewater is a relevant and important issue today, and ion exchange technologies are presented as an interesting alternative. However, these technologies face significant technical and economic challenges that need to be addressed for large-scale application. This master's thesis aims to assess the techno-economic feasibility of ion exchange technologies for the recovery of nutrients from wastewater and to identify the main challenges and opportunities for their application.

1.1. Objectives

The main objective of this work is to evaluate the economic viability of the application of ion exchange technologies for the recovery of nitrogen and phosphorus from municipal wastewater. To achieve this objective, the following specific objectives are proposed:

1. To carry out a literature review to identify and compile key operational parameters related to the operation of the wastewater treatment plant.
2. To carry out the pre-design and mass/energy balances of a ion exchange system to recover nitrogen and phosphorus from municipal wastewater to obtain the necessary data for the economic evaluation.
3. To identify different alternatives that combine ion exchange technologies with other membrane and precipitation technologies to obtain high quality fertilisers ready for agricultural application.
4. To determine the economic viability of the application of ion exchange technologies in the recovery of nitrogen and phosphorus, considering the costs associated with the process and the income generated from the sale of the fertilizer products obtained.
5. To perform a sensitivity analysis of the most relevant design and economic parameters to identify the key factors affecting the economics of the nutrient recovery process. In addition, the impact of variations in equipment costs, operating expenses and sales prices of the products obtained have been evaluated.

1.2. Methodology and scope

The methodology used in this study was based on an exhaustive literature research on ion exchange processes and complementary technologies for the recovery of nutrients in the form of fertilisers. From the data collected, key operational parameters were selected with the aim of achieving maximum system efficiency. The corresponding material and energy balances were carried out, and all the data necessary to perform the economic analysis and the sensitivity analysis of the key aspects of the project were collected.

Regarding the scope of the project, it is important to note that this study should be understood as an exploratory research approach. In this context, the work aims to prospect nutrient recovery treatments in wastewater using ion exchange technologies, as well as to assess the feasibility of the system. The aim is to analyse the relevant technical and economic aspects to determine the efficiency and feasibility of the process.

Although this study provides an initial insight into the application of ion exchange technologies in nutrient removal and recovery, further research is recommended to investigate specific aspects and further optimise the system.

2. State of the art

Due to global population growth, economic development and urbanisation, wastewater treatment is an increasingly important concern. Wastewater is the result of human, industrial and agricultural activities and contains a wide variety of pollutants such as organic matter, suspended solids, nutrients, heavy metals, chemicals, and pathogenic microorganisms (Chen et al., 2020).

The composition of wastewater varies significantly depending on its origin and season. For example, wastewater from domestic sources usually contains high concentrations of organic matter, nutrients (e.g., nitrogen and phosphorus), fats, and oils (Almeida et al., 1999). On the other hand, wastewater from industrial sources often contains specific pollutants related to the specific activity of each industry, such as chemicals or heavy metals, among others (Rodríguez-Vidal et al., 2022).

In terms of wastewater treatment technologies, there are several processes that can be classified into physical, chemical, and biological, each of which has its advantages and disadvantages depending on the pollutants to be removed (Crini & Lichtfouse, 2019).

Physical processes are based on the physical separation of pollutants in wastewater and include filtration, sedimentation, and flotation. Filtration removes particles and suspended solids by passing wastewater through a porous medium. On the other hand, sedimentation is used to separate heavy particles, such as suspended solids, by the force of gravity. Flotation involves the formation of air bubbles that attach themselves to suspended solids, causing them to float to the surface of the water where they can be easily removed; this technology is efficient at removing small particles but requires high costs in terms of energy (Crini & Lichtfouse, 2019).

Chemical processes are based on the addition of chemicals that allow the removal of contaminants. These processes include chemical precipitation, adsorption, disinfection, coagulation-flocculation, and oxidation (Samer, 2015). Chemical precipitation is used to remove inorganic compounds such as heavy metals and phosphates by the addition of chemicals, forming insoluble precipitates. The main advantage of this technique relies on the simple equipment needed, while the main disadvantage is the high consumption of chemicals (Oncel et al., 2013). Adsorption is used to remove organic and inorganic compounds using adsorbent materials such as activated carbon and zeolites. One of the advantages of these technologies is the wide variety of commercially available products and the high efficiency of the process, while the main disadvantage is the high chemical cost and the cost of materials (Crini & Lichtfouse, 2019). On the other hand, coagulation-flocculation involves the addition of a coagulant to form flocs of particles that can be easily removed (Aguilar, 2002). The main advantage of this technology relies on the simplicity of the process while its main disadvantage is the high volume of sludge generated. At this point it is also worth mentioning the existence of other advanced physico-

chemical water treatment processes such as air stripping, ion exchange, ultrafiltration, reverse osmosis and electrodialysis. Each of these processes removes specific pollutants of interest (Crini & Lichtfouse, 2019; Samer, 2015).

Biological processes are based on the use of microorganisms to remove pollutants in wastewater. Among the most used technologies are aerobic treatment; where the biodegradable organic matter is removed through the effect of aerobic microorganisms and anaerobic treatment; which is a process in which microorganisms break down organic matter in the absence of oxygen, generating biogas as a by-product. This process is efficient in reducing the organic load and can be used as an initial treatment stage or to treat settled sludge. On the other hand, the activated sludge process is based on the mixing of a dense bacterial population under aerobic conditions, which results in the degradation of the available organic matter, after which the activated sludge is separated from the treated water in a clarifier. Finally, biological nutrient removal allows the removal of phosphorus or nitrogen, depending on the microorganisms used. For phosphorus removal, microorganisms called "phosphate accumulators" are used to capture and store the phosphorus present in the wastewater. In the case of nitrogen removal, nitrifying and denitrifying microorganisms are used, which convert ammoniacal nitrogen into nitrate and then into gaseous nitrogen, respectively (Samer, 2015).

In practice, wastewater treatment technologies are chosen according to the specific characteristics of the water to be treated and the treatment objectives set. In general, after primary water treatment, i.e., physical water treatment, the water contains large amounts of dissolved material that must be removed, so the water is sent to secondary treatment where the biological treatments mentioned above take place. Finally, in chemical treatment, or tertiary treatment, contaminants such as heavy metals are removed, although a portion of the contaminants will remain unaffected (Samer, 2015).

On the other hand, among the emerging technologies for nutrient recovery from wastewater, ion exchange technologies stand out as a widely used technology that can reduce water pollution and provides valuable resources such as nitrogen and phosphorus for agriculture and other uses.

Ion exchange technology uses resins to selectively remove nutrients from wastewater. The choice of resin depends on the type of nutrient to be recovered and the specific conditions of the water to be treated. Briefly, the mechanism is based on the selective removal of ions contained in the water by exchanging them for other ions present in the ion exchange resin. In the case of nitrogen, there is a growing interest in the use of zeolites as adsorbent material to achieve its removal due to its high selectivity and capacity for NH_4^+ (Canellas-Garriga, 2018). There is a wide variety of zeolites, both synthetic and natural, which exhibit different capacities and selectivity towards ammonium depending on parameters such as the initial ammonium concentration or the presence of other ions in solution, among others. For example, Mackinnon et al., (2003), studied the use of synthetic mesolite treating a stream from anaerobic digesters with an initial ammonium concentration of 500-1000 mg L⁻¹ and

obtained an operational capacity of 45-50 mg g_{resin}⁻¹. Mc Veigh & Weatherley, (1999), studied the use of clinoptilolite when treating a synthetic mono-component solution with an initial concentration of 25-32 mg L⁻¹ of ammonium, obtaining an operational capacity of 32 mg g_{resin}⁻¹. Cooney et al., (1999), studied the use of Australian clinoptilolite to treat a secondary effluent with an ammonium concentration of 25-45 mg L⁻¹, obtaining an operational capacity of 2.3-2.8 mg g_{resin}⁻¹. On the other hand, there are several resins that can be used for phosphorus removal. For example, Martin et al., (2009) compared the performance of a resin of hydrated ferric oxide nanoparticles dispersed within the pore structures of polymeric anion exchanger beads (HAIX) with the standard resin Amberlite IRA-410, concluding that HAIX shows much higher capacity than a comparable strong base anion exchanger when treating a real effluent stream. There are several authors who tested the performance of metal oxide loaded sorbents. For example, Liu & Zhang (2015) studied Zr(IV) loaded chitosan beads (ZCB) and obtained a capacity of 61.7 mg g_{resin}⁻¹ when treating a synthetic solution with an initial phosphate concentration of 30 mg L⁻¹. Liu et al. (2016) studied the performance of zirconium (IV) loaded chitosan particles obtaining a capacity of 71.68 mg g_{resin}⁻¹ when treating a synthetic solution with a phosphate concentration of 10-300 mg L⁻¹. Similarly, An et al. (2014) used copper loaded chitosan beads and obtained a capacity of 70 mg g_{resin}⁻¹ when treating a synthetic solution with an initial phosphate concentration of 50 mg L⁻¹.

The regeneration stage is essential in the operation of ion exchange technologies since the resins used can recover their ion exchange capacity after being saturated with the nutrients of interest. For resin regeneration, chemical solutions are used to dissolve the nutrients adsorbed on the resin and replace them with other ions so that the resin can be used again without the need to purchase a new one. The regeneration process depends on several factors such as the type of resin, the concentration and type of regeneration solution, the contact time, and the temperature. According to some studies, saline solutions such as NaCl are generally used to regenerate strong acid cationic resins while HCl or H₂SO₄ can be used to regenerate strong and weak acid cationic resins. However, it has been found that the use of NaOH can improve regeneration efficiency and provide a higher degree of nutrient recovery (Deng et al., 2014). Canellas-Garriga, (2018) evaluated the use of KCl and NaCl for regeneration of mesolite saturated with ammonium ions. It was obtained that with KCl regeneration the efficiency was 72 to 94% while with the use of NaCl achieved efficiencies of 64 to 68%. In addition, alkaline regeneration at a basic pH through the addition of NaOH decreased the concentration of KCl required for regeneration compared to NaCl, contributing to a saving in terms of regenerant cost. In other studies, the regeneration of phosphorus-loaded ion exchange resins was evaluated using different regenerating solutions. For example, Bottini & Rizzo, (2012) obtained an efficiency of 95% when regenerating a HAIX with a 1M NaOH solution while Boyer et al., (2011) used a 2% NaCl and 2% NaOH solution obtaining an efficiency of 80%. In summary, the regeneration stage is crucial in ion exchange technology. The choice of regeneration solution significantly influences the efficiency and nutrient

recovery as well as waste generation, so it is important to pay special attention to the choice of the optimum regenerant.

Once the nutrients have been recovered from the ion exchange resins by the regeneration solution, they must be recovered in the form of phosphorus and nitrogen fertilisers. For this purpose, there are different technologies where different products can be obtained depending on the technology, the operating parameters and the chemical compounds used. One of the most used technologies to recover the nutrients is crystallisation by adding chemicals such as calcium and magnesium to precipitate in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$), potassium struvite ($\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$) and hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2(\text{s})$). All these products can be used as slow-release fertilizers (Münch and Barr, 2001; Alan O 'Neal, 2013). On the other hand, membrane technologies are an alternative that is currently gaining special interest for ammonia recovery compared to other conventional processes such as strippers, scrubbers, and deaeration systems. Liquid-liquid membrane contactor (LLMC) is a separation technique that uses a membrane to permeate gaseous species contained in a feeding liquid phase and captures them using a liquid receiving phase that reacts with the gaseous species (Ulbricht et al., 2013). As a rule, the ammonia-containing solution is fed through the shellside of the hollow fibre membrane while an acidic solution (usually H_2SO_4) is fed through the lumenside in countercurrent. The difference in ammonia gas concentrations between the two solutions is the driving force that allows the ammonia to be transferred across the microporous membrane. Ulbricht et al., (2013) concluded that the LLMC process is comparable to conventional gas transfer technologies and that the technology has significant advantages that can reduce CAPEX and OPEX under certain operating parameters.

In addition to ion exchange technologies, other technologies are available to remove/recover nutrients from wastewater. Biological nitrogen removal is an alternative that consists of nitrification-denitrification by the action of ammonium oxidising bacteria (AOB) that oxidise ammonium and nitrite to nitrate, followed by reduction to nitrogen gas by facultative heterotrophic bacteria. However, nitrogen removal should be moved away from nitrification/denitrification as the process is very energy intensive (Winkler & Straka, 2019). Air stripping of ammonia is another technology that is widely used for wastewater pre-treatment. The process takes place in stripping tanks or packed towers and the two major disadvantages are scaling and fouling on the packing surface and the low stripping efficiencies. Bioelectrochemical systems (BES) combine oxidation-reduction reactions in which the release/capture of electrons from an electrode is facilitated by microorganisms. This technology can be integrated with conventional nitrogen recovery processes such as membrane stripping and precipitation. The potential of BES is relevant, but it is currently a technology under experimental development (Kuntke et al., 2018). For phosphorus recovery and removal there are also several alternatives available. Enhanced biological phosphorus removal (EBPR) is a configuration applied to activated sludge systems for phosphate removal where polyphosphate accumulating organisms (PAOs) accumulate volatile fatty acids under anaerobic conditions. Subsequently, in the aerobic phase, these

bacteria accumulate large amounts of polyphosphate enhancing phosphorus removal. Chemical precipitation is another alternative based on the addition of metallic salts of iron or aluminium producing a precipitation in the form of phosphates. The precipitate is removed from the water by sedimentation, filtration or flotation processes and its main disadvantage is based on the high costs of the reagents and the generation of sludge that must be properly managed (Nassef, 2012).

Techno-economic assessment is a key step in the selection of wastewater treatment and nutrient recovery technologies to determine the feasibility of a technology in cost-benefit terms. There are different criteria for assessing the efficiency and economic viability of nutrient recovery technologies, including the cost of the process, production capacity, quality of the product obtained, lifetime of the treatment materials and environmental impacts. In the case of ammonium recovery by ion exchange technologies, different techno-economic evaluation studies have been carried out to determine the efficiency and economic viability of this technology. For example, Canellas-Garriga, (2018) evaluated the key parameters that influence the economic viability of using zeolites for ammonia removal from wastewater and concluded that the use of mesolite appears economically feasible in comparison to using a nitrifying submerged aerated filter if the brine is effectively managed. This means that the brine (i.e., the regenerant containing the recovered nutrient) should be reused as far as possible including a local cleaning system. Regarding phosphorus recovery, Muhammad, (2017) evaluated the use of hybrid resin in fixed bed IEX systems concluding that it is a viable technology as a tertiary treatment for phosphorus removal capable of significantly reducing the phosphorus concentration in the effluent. In addition, the regenerant cleaning strategy will depend on the treatment capacity. For small cities (2000 PE), the most economical strategy would be to have a mobile clean-up system whereas for medium size water works (20000 PE) having an on-site clean-up system would be more beneficial.

Besides techno-economic assessment, other tools have been used to evaluate the environmental impacts of nutrient recovery technologies, such as the life cycle analysis (LCA) (Guida et al., 2021). This tool allows to assess not only the direct costs associated with the treatment process, but also the long-term environmental impacts, allowing to select the best treatment option.

The current trend in the use of ion exchange technologies is based on the "cradle to cradle" approach that considers wastewater treatment as an opportunity to recover and reuse valuable resources. In this direction, the implementation of emerging technologies, such as reverse osmosis or advanced oxidation, should be explored as they are technologies that can offer advantages in terms of efficiency and treatment capacity. However, nutrient recovery technologies and, in particular, ion exchange technologies face important challenges, such as the scaling of the columns or the presence of competitive ions in the wastewater (Canellas-Garriga, 2018; Yen Nguyen, 2017).

3. Ion exchange theory and mechanism

The theory of ion exchange is based on the ability of certain materials to exchange ions from an aqueous solution for other ions of similar charge but of different origin. In other words, it can be described as a chemical reaction between a relatively insoluble substance and a solution. The exchanged ions will have the same electric charge. In cation exchange, the positively charged ions are substituted while in anion exchange, the negatively charged ions are exchanged (Kumar & Jain, 2013).

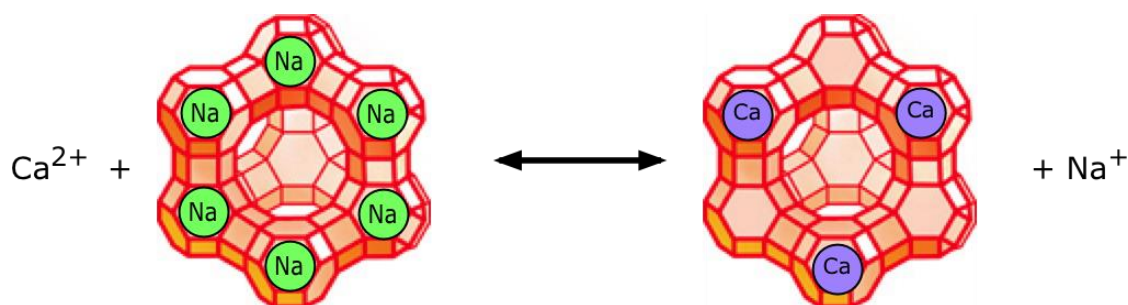


Figure 1. Ca^{2+} exchange onto Na-typed zeolites. (Hard water and water softening)

Figure 1 schematizes the ion exchange mechanism in zeolites. Ca^{2+} dissolves in water until it comes into contact with zeolites. Na^+ , which was bound to the zeolite, dissolves in water and calcium takes its place in the zeolite (Rozic, 2000).

The different resins used in ion exchange have a different affinity for certain types of ions. In addition, the ion exchange capacity of a resin depends on several factors, such as the type and amount of electrically charged functional groups in the resin, the charge and size of the ions being exchanged, the concentration and pH of the aqueous solution, the temperature, and the flow rate of the solution through the resin (Demir et al., 2002). These factors must be carefully considered in the design and operation of an ion exchange system to ensure optimum efficiency.

As for the ion exchange mechanism, it shares basic characteristics very similar to the adsorption mechanism. Both operations remove specific substances from an aqueous solution by means of a porous substance. However, adsorption only removes substances from a solution while ion exchange introduces new substances into the liquid. Another difference between the systems is that with adsorption, neutral substances can be removed, whereas with ion exchange the substance must be electrically charged to be removed (Inglezakis & Pouloupoulos, 2006).

The similarity between the two systems means that some kinetic principles are also the same. The main mechanism that aids elimination is diffusion, which is described as the transport of molecules or ions from a region of higher concentration to a region of lower concentration. In the case of ion exchange, this mechanism can be divided into the following stages (Mikkers, 2009):

- 1) Transport of the specific substance from the bulk liquid to the outer surface of the adsorbent material by molecular diffusion (film diffusion). In the process, a layer of ions forms on the surface of the particles, which involves mass transfer resistance for the ions in solution to bind to the ion exchange material. The concentration gradient in this film is the driving force for this type of diffusion.
- 2) Transport of ions from the surface to the inside of the particle by diffusion within the pore-filling liquid. This is called internal diffusion.
- 3) Adsorption of ions on the active sites on the inner surface of the pores.

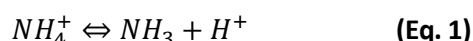
There are different stages that can limit the rate, and depending on the specific circumstances, one of these stages will determine the rate of the process. If step 3 is not rate controlling, then step 1 or 2 must do so. This will depend on several factors (Inglezakis & Poulopoulos, 2006):

- Concentration in the liquid phase (higher concentration means higher driving force in the film layer)
- The ion exchange capacity of the material (higher capacity means higher driving force in the exchanger)
- Particle size (smaller particle size means shorter pore mass transfer distances)
- The aperture of the ion exchanger structure (larger pores mean less clogging and therefore easier access)
- Amount of liquid agitation (agitation of the liquid facilitates mixing of ions around particles)
- Selectivity of the exchanger (high selectivity accelerates the adsorption of certain ions)

Finally, based on the above factors, it can be determined which mechanism is the rate controlling one. However, to be completely sure, an interruption test can be performed, which is a technique used to evaluate the efficiency and capacity of ion exchange materials.

3.1. Ammonia removal from municipal wastewater

Ammonia is a highly soluble gas with a Henry's law constant of $5.53 \times 10^{-4} \text{ mol L}^{-1} \text{ Pa}^{-1}$ so that its solubility is 900 g L^{-1} at $0 \text{ }^\circ\text{C}$ and 400 g L^{-1} at $300 \text{ }^\circ\text{C}$ (Canellas-Garriga, 2018). Ammonia is a weak base that dissociates in water to form a pH-dependent equilibrium with its ionic form, ammonium. The distribution of ammonia species as a function of pH is shown below, using the chemical equilibrium (equation 1):



The equilibrium shifts to the right side when the pH is low and to the left when is high. In general, at pH 7, the proportion of ammonia-N in the form of NH_3 is very low and almost all ammonia nitrogen is

present in the form of NH_4^+ . At pH around 8, the proportion in the form of NH_3 is 10% or less and at pH slightly above 9, the proportion is around 50%. Once the pH is >11 , all ammonium ions in solution are in the molecular form of ammonia. According to these data, the predominant form in the wastewater will be ionic ammonium as the pH of the wastewater is between 6.5 and 8 (Metcalf & Eddy, 2003), which allows its removal with ion exchange technologies.

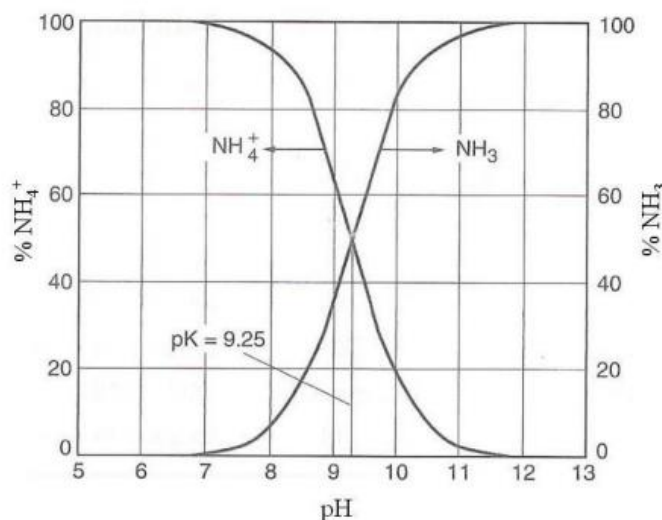
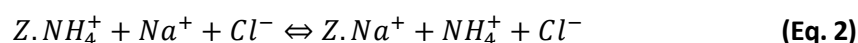


Figure 2. Ammonium and ammonia distribution as a function of pH. (Metcalf & Eddy, 2003)

Ion exchange is a physicochemical process carried out in an ion exchange column, which is filled with an ion exchange resin. Ammonia ions (NH_4^+) are selectively exchanged for other ions of equal charge residing in the medium (e.g., Na^+ or K^+), thus maintaining a charge balance as describes in equation 2:



Where; $Z.\text{NH}_4^+$ is the ammonium in the solid, Na^+ is the sodium released from the solid, Cl^- is the chlorine in the liquid, $Z.\text{Na}^+$ is the sodium in the solid and NH_4^+ is the ammonium in the liquid.

The efficiency of the ammonium cation exchange process depends on several factors, such as the initial concentration of ammonium in solution, the amount and type of resin used or the contact time and the pH of the solution. In addition, other ions in solution may compete with ammonium for adsorption onto the resin. However, selectivity allows ammonium to be preferentially removed over other species such as Ca^{2+} or Mg^{2+} . Once the resin is saturated, it is regenerated using high-strength ionic brines, where the regenerant ion replaces the NH_4^+ adsorbed on the solid by releasing it into the liquid phase (Canellas-Garriga, 2018; Deng *et al.*, 2014; Mackinnon *et al.*, 2003; Mackinnon *et al.*, 2010).

3.1.1. Zeolites as a removal media

Among all the different materials that have shown promising features for ammonium removal, zeolites are the most widely used. Zeolites are microporous aluminosilicate minerals with the ability to hydrate and dehydrate in a reversible manner and can be found naturally or formed synthetically (Moshoeshoe et al., 2017). Natural zeolites are found in sedimentary, volcanic, and metamorphic rocks resulting in inconsistency and variability in terms of purity, porosity, pore diameter, capacity, and other physical and chemical parameters (Pérez-Botella et al., 2022; Canellas-Garriga, 2018). On the other hand, the production of synthetic zeolites has been extensively studied by several authors. For example, Mackinnon et al., (2010) studied the production of zeolite N from a variety of kaolinites and montmorillonites at low temperature (< 100 °C) in a continuously stirred reactor (CSTR). The synthetic production of these materials is very large as consistent zeolites with higher selectivity towards the ion of interest can be obtained (Mackinnon et al., 2010).

Due to the microporosity, zeolites have high surface areas and have been widely used in applications such as catalysis, ion exchange and other separation processes. Specific zeolites can be differentiated by chemical composition (Si/Al), pore size and pore topology. In structure, they consist of an infinitely extensive three-dimensional network of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra linked to each other by sharing of oxygen atoms (Breck, 1974). Its structure can be considered an inorganic polymer consisting of tetrahedral TO_4 units, where T is a Si_4^+ or Al_3^+ ion and each O atom is shared between two T atoms. The primary building unit of zeolites is the tetrahedron and the secondary building units (SBU) are the geometrical arrangements of the tetrahedra, which can be polyhedra or cubo-octahedra structures. Structures can be formed by repeating SBUs and according to them zeolites can be classified into eight different groups (Georgiev et al., 2009).

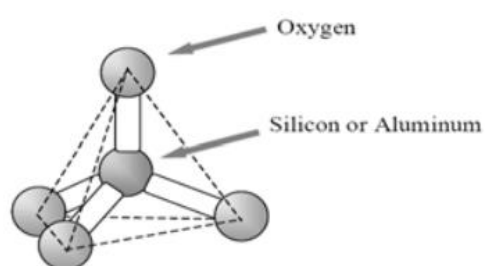


Figure 3. Primary building unit of zeolite structure. (Georgiev et al., 2009)

The open zeolite structure consists of many interconnected channels of size 0.3-20 Å occupied by cations and water molecules. Each AlO_4 tetrahedron in the structure has a net negative charge which is balanced by a cation (e.g., Na^+ , K^+ or Ca^{2+}). The voids of zeolites play an essential part as the flexibility and size of the cavities allow water molecules and cations to pass through them. In this way, cations undergo exchange and maintain the neutrality of the structure when a central Al ion is present

(Canellas-Garriga, 2018). Therefore, since neutrality must be fulfilled, the sum of Al centre ions will be equal to the sum of exchangeable cations defined as the ion exchange capacity (CEC) (Palaban, 2001).

Selectivity is the affinity of certain materials for certain ions. The explanation for selectivity is based on combinations of materials and ions in relation to ion radio (molecular sieving), ion hydration energies and electrostatic binding energies (Cooney *et al.* 1999; Hankins *et al.*, 2005; Metropoulos *et al.*, 1993). However, to explain the difference in selectivity between different materials it is necessary to focus on the properties of zeolites, such as Si:Al ratio, Al distribution, type of neutralising alkaline cations and zeolites hydration (Canellas-Garriga, 2018).

The Si:Al ratio of a zeolite is a very important parameter since Si-O bonds have an electrostatic bond of 1 while Al-O bonds have an electrostatic bond of 0.75 (Armbruster, 2021). Therefore, depending on the type of species that is bonded to the oxygen will result in a different sum of bonds, which will have an impact on the overall charge density within the zeolite structure with this increasing as the Si:Al ratio decreases. Wang *et al.*, (2008) studied ammonium ion exchange in natural and synthetic zeolites and concluded that zeolites with relatively low Si:Al molar ratio (1.8-2.3) show higher selectivity towards low charge cations such as Na^+ or NH_4^+ . In addition, the amount of Al in the zeolite has an impact on hydrophobicity, becoming more hydrophobic as the Si:Al ratio increases (Li *et al.*, 2013; Ockwig *et al.*, 2008).

The distribution of Al in the zeolite structure also plays an important role in selectivity. For example, Nakamura *et al.* (2013) studied the cation adsorption selectivity mechanism of zeolites and found three crucial conditions for the selective exchange of Na^+ ions for Cs^+ : i) micropores with a radius of about 3 Å, ii) a low Si:Al ratio, and iii) a uniform distribution of Al atoms around each micropore.

3.1.2. Use of different zeolites for ammonia removal from wastewater

Several typologies of zeolites (both natural and synthetic) have been studied for the removal of ammonium from wastewater, including Clinoptilolite, Mesolite (Zeolite-N) and Modernite. Each type of zeolite has differences in terms of capacity as the composition and purity of the materials is different depending on the part of the world from which they are extracted. In addition, the capacity is also influenced by competition with other ions that are also present in the water. For example, Langwaldt, (2008) showed that the selectivity of various cations in Clinoptilolite is as follows: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Li}^+$. A similar sequence was found by Dryden & Weatherley, (1987): $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. As can be seen, with respect to ammonium, Clinoptilolite shows less affinity for all cations present in water except potassium. This may be positive since potassium is found in low concentrations compared to other species (Mikkers, 2009). Several studies on different zeolites have shown small differences in selectivity sequences, so the sequence is different depending

on the type of zeolite chosen. Table 1 shows the sequences obtained by several authors depending on the type of material used.

Table 1. Studies on different zeolite selectivity sequences.

Material	Source of water	Equilibrium Capacity (meq NH_4^+ g zeolite $^{-1}$)	Initial concentration (mg NH_4^+ L $^{-1}$)	Selectivity sequence	Reference
Natural Clinoptilolite	Multi-component (NH_4^+ , Ca^{2+} and Na^+) synthetic solution	0.47	2,880	$\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+}$	Hankins et al., 2005
Clinoptilolite	Two-component: synthetic solution (NH_4^+ , Ca^{2+})	0.57	200	$\text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$	Weatherley & Miladinovic, 2004
Modernite	Two-component: synthetic solution (NH_4^+ , Mg^{2+})	0.61	200	$\text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$	Weatherley & Miladinovic, 2004
Chinese natural zeolite	Mono-component: NH_4^+ synthetic solution	0.39	50	$\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$	Lei et al., 2008
Clinoptilolite	Multi-component: Real wastewater (secondary effluent)	0.2 to 0.5	7 to 40	$\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+}$	Mc Veigh & Weatherley, 1999
Zeolite A (Na-A, K-A and Ca-A)	Mono-component: NH_4^+ synthetic solution	1,2, 1 and 0.9	1,800	$\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{NH}_4^+$	Metropoulos et al., 1993

Available studies on synthetic zeolites are more limited. However, MesoLite (Zeolite-N) has been studied by several authors and has been shown to have a high capacity and selectivity towards ammonium. Mackinnon et al., (2003) showed that MesoLite has a high capacity for ammonium removal, achieving >90% removal while Thornton et al. (2007) demonstrated that MesoLite has a capacity of 72 mg g $^{-1}$ when treating a mono-component solution of 1000 mg L $^{-1}$ of ammonium.

In terms of dynamic studies using MesoLite, two studies should be highlighted. Mackinnon et al., (2003) studied a stream with an initial concentration of 500-1000 mg L $^{-1}$ NH_4^+ and obtained operational capacities of between 45-50 mg g $^{-1}$ NH_4^+ while Thornton et al. (2007b) carried out the study with an initial concentration stream of 600-650 mg L $^{-1}$ NH_4^+ and an EBCT of 12 minutes, obtaining an operational capacity between 27-39 mg g $^{-1}$. Other similar studies using Clinoptilolite can be found in table 2. For example, Cooney et al., (1999) used Australian Clinoptilolite to treat a real secondary effluent with an initial concentration of 25-45 mg L $^{-1}$ NH_4^+ and obtained a maximum operational capacity of 2.8 mg g $^{-1}$. Hlavay et al. (1982) used Hungarian Clinoptilolite in their studies to treat wastewater with an initial concentration of 17-45 mg L $^{-1}$ NH_4^+ and obtained a maximum operational capacity of 4.17 mg g $^{-1}$. These studies have proven the efficacy of zeolites for the removal of ammonium

from wastewater. However, the main challenges of this technology are based on the need to reduce the solids concentration to avoid clogging, the high cost of regeneration and the management of the regenerant solution (Hedström, 2001; Liberti et al., 1981).

Table 2. Dynamic studies for ammonium removal using different zeolites.

Material	Source of water	Operational capacity (mg g⁻¹)	Initial concentration (mg L⁻¹)	Breakthrough concentration (mg L⁻¹)	Reference
Synthetic zeolite: Mesolite	Real side streams from anaerobic digesters	45-50	500-1,000	50	Mackinnon et al., 2003
Synthetic zeolite: Mesolite	Real side streams from anaerobic digesters	27-39	600-650	50	Thornton et al., 2007b
Australian Clinoptilolite	Real secondary effluents	2.3-2.8	25-45	5	Cooney et al., 1999
Clinoptilolite (Hungarian)	Wastewater	4.13-4.17	17-45	2	Hlavay et al., 1982
Synthetic zeolite	Mono-component NH ₄ ⁺ (synthetic solution)	17.5	40	2	Malovanyy et al., 2013

3.1.3. Regeneration of zeolites

Zeolite regeneration is an important step in ammonium recovery by ion exchange. Once the effluent reaches the maximum allowable ammonium concentration, an equilibrium is established between the ammonium concentration in the feed water and on the zeolite. The zeolite is exhausted due to reaching adsorption capacity and, therefore, the zeolite is not able to adsorb more ammonium ions. The zeolite must be regenerated in order to restore its ion exchange capacity so that it can be reused in future cycles.

Regeneration can be carried out in different ways. In the case of ammonium, chemical regenerations are carried out in order to make the zeolite binding sites available again. This is achieved by using a chemical solution to desorb ammonium and other ions.

Regarding the regenerant solution that can be used, there are many studies in the literature dealing with zeolite regeneration for ammonium recovery. For example, the study by Liberti et al. (1981) used a 0.6 M NaCl solution for the regeneration of Clinoptilolite while other authors such as Ashrafizadeh et al. (2008) and López-Vigil et al. (2006) reached high regeneration efficiencies after using NaCl at different concentrations. Other authors, such as Thornton et al. (2007b) used a 5% NaOH solution with a flow rate of 5 BV h⁻¹ for 4 hours. However, when regenerating at high pH, special care must be taken since high pH can damage the zeolite and there is also the possibility of calcium precipitation on the zeolite or in the pores (Mikkers, 2009).

Deng et al., (2014) used a mixture of NaCl and NaOH as regeneration solution and concluded that alkaline regeneration at pH 12 significantly reduced the concentration of NaCl required from 80 to 10 g L⁻¹, which allows savings in terms of chemicals' consumption.

Another study by Canellas-Garriga, (2018) concluded that KCl is a more effective regenerant than NaCl when MesoLite is used as a zeolite. The regeneration efficiencies were between 72 and 94% for KCl and between 64 and 68% for NaCl. Furthermore, KCl remained effective down to 0.1 M concentrations while NaCl achieved the same regeneration efficiency but using 1.0 M concentrations. It is also concluded that there is no difference between performing regeneration at pH 9 or 12, however, at pH 12 effective regeneration can be performed without the inclusion of brine, such as NaCl or KCl.

On the other hand, Hedström, (2001) concluded that low regeneration rates (<5 BV/h) have a negative effect on regeneration time as it takes much longer to regenerate the same amount of zeolite.

In summary, zeolite regeneration is a very important step in ammonium recovery by ion exchange. It is important to control the regeneration parameters, such as regeneration solution concentration, contact time and temperature, to avoid zeolite degradation and to optimise the efficiency of the operation.

3.2. Phosphate removal from municipal wastewater

The principle of ion exchange can also be applied to the removal of P from wastewater and may be a particularly suitable operation for use at decentralised sites (Zhao & Sengupta, 1998). Although ion exchange phosphorus recovery technology has not been as well studied or applied as other physicochemical P removal methods, the highly selective nature of some exchange media justifies its consideration (Bunce et al., 2018).

The predominant form of P in wastewater effluents is anionic. Phosphate ions are reversibly exchanged between the wastewater and the ion exchange resin, providing simultaneous removal and recovery of this nutrient (Martin et al., 2009). Immobilised particles of a metal cation often form the polymeric exchange base on which P-selective nanoparticles (e.g., ferric oxide) are placed (Zhao & Sengupta, 1998). This approach allows P anions in wastewater to be selectively captured from other competing ions, such as sulphates or chlorides. However, this is difficult due to the realistically low concentration of phosphate in wastewater effluents, compared to other competing species (Bunce et al., 2018).

The performance of traditional ion exchangers is governed by the valence and weight of the ion in question. However, due to the low concentration of phosphate ions in wastewater, early attempts to apply this technology were unsuccessful. More recent studies have succeeded in improving the

efficiency by pre-treating the ion exchange media to increase the selectivity towards phosphate ions (Martin et al., 2009).

3.2.1. Media for phosphorus removal

Different materials are available to remove phosphorus from wastewater and various media such as clay, furnace slag, fly ash, metal oxides and modified hybrid materials have been studied.

Non-metallic oxides made from by-products of industrial processes (slag, ochre, fly ash, shale) have proven to be an effective and cheap alternative for phosphorus removal (Westholm et al., 2014). In this case, the media contain relatively high concentrations of iron oxide, aluminium and calcium which have proven to be effective. Zheng & Liu., (2004) studied the capacity of iron oxide and observed that its capacity decreased from 8.6 mg L^{-1} to 4.6 mg L^{-1} as the pH increased from 3.2 to 9.5, respectively. The medium showed poor desorption due to the strong binding between phosphorus and iron tailings. Phosphorus removal from these materials is complex and is hypothesised to occur through a combination of precipitation and adsorption mechanisms (Muhammad, 2017).

Metal oxides are another media option for phosphorus removal due to their large surface area and preferential surface properties. Multiple trials have been conducted using lanthanum, ferric, magnesium, titanium, zirconium, aluminium, and copper oxides, in single, binary, and tertiary forms. The capacity of these materials increases when using binary and tertiary metal oxide complexes. For example, the capacity of lanthanum oxide was measured ($46.9 \text{ mg PO}_4^{-3} \text{ g}_{\text{media}}^{-1}$) and compared to when it was used as part of a ferric oxide-magnesium-lanthanum complex, resulting in a final capacity of $85 \text{ mg g}_{\text{media}}^{-1}$ (Xie et al., 2014; Yu & Paul Chen, 2015). However, regeneration over multiple operating cycles has shown a reduction in the capacity of the ferric oxide-magnesium-lanthanum metal complexes. This must be considered for the long-term operability of the materials (Muhammad, 2017).

Although metal oxides have been shown to have great potential for phosphorus removal, there are problems with the operation that limit their application. For example, when used in powder form, the fine particles aggregate in the water, reducing its surface area and generating large pressure losses in the operation (Pidou et al, 2009). To solve this problem, the metal oxide particles are dispersed in a series of materials that act as skeletons such as activated carbon, ion exchange resins, silicates, zeolites, and chitosan (Muhammad, 2019).

Liu & Zhang (2015) studied Zr (IV) loaded chitosan beads and obtained a capacity of $61.7 \text{ mg g}_{\text{media}}^{-1}$ when treating a stream with a concentration of 30 mg L^{-1} phosphate. On the other hand, An et al. (2014) studied copper loaded chitosan beads and obtained a capacity of $70 \text{ mg g}_{\text{media}}^{-1}$ when treating a stream with a concentration of 50 mg L^{-1} phosphate. It has been concluded that the inclusion of metal

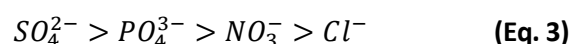
oxides in the structure does not increase the capacity but does increase the selectivity towards phosphate in the presence of other components (Sowmya and Meenakshi, 2013; Dai et al., 2011).

Silicates have also been used as structures due to their large surface areas and controlled pore diameters. Among the metal oxide particles, iron, lanthanum, zirconium, aluminium, and titanium have been studied dispersed in different forms and obtaining different phosphorus removal values. For example, Huang et al., (2015) studied silica spheres loaded with lanthanum and obtained a capacity of $42.8 \text{ mg g}_{\text{media}}^{-1}$ when treating water with a concentration of $2\text{-}50 \text{ mg L}^{-1}$ of PO_4^{3-} .

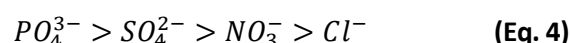
Activated carbon has also been widely used for the removal of a wide range of pollutants due to its high porosity. The parameter that has the highest impact on the operation of activated carbon is pH as phosphate removal decreases with increasing pH (Shi et al., 2011). This indicates that phosphorus removal occurs mainly at the base of the carbon. Zhang et al. (2012) studied lanthanum-loaded activated carbon fibre and obtained a capacity of $10.5 \text{ mg g}_{\text{media}}^{-1}$ when treating water with a concentration of $10\text{-}70 \text{ mg L}^{-1}$ phosphate.

3.2.2. Use of different metal oxides and ion exchange resins for phosphate removal from wastewater

Ion exchange resins are the most commonly used systems due to their high physical and chemical stability, easy handling and the possibility of multiple reuses through regeneration. Like other media, resins also suffer from selectivity problems mainly due to the presence of sulphate (due to its higher concentration and charge), so their adsorption is more favourable than that of phosphate. An et al. (2014) reported that the affinity sequence is as follows (equation 3):



However, the inclusion of metal oxides such as ferric, copper and zirconium allows for increased selectivity towards phosphate as it is a strong ligand towards these materials and forms inner-sphere complexes through Lewis-acid base and electrostatic interactions. On the other hand, sulphate is a weak ligand and forms outer-sphere complexes with the metal oxide via electrostatic interaction. As a result, sorbents loaded with metal oxides show the affinity sequence described in equation 4 (An et al., 2014):



Despite the increased selectivity towards phosphate, the accumulation of sulphate ions on the sorbent surface has been found to weaken the electrostatic attraction of phosphate ions and metal oxide, resulting in a decrease in capacity (Liu et al., 2015). The most used embedded metal oxide is ferric, for which commercial availability is feasible (Muhammad, 2019).

There are multiple publications studying the operation of ferric-loaded ion exchange resins using different types of effluents. For example, Pan et al. (2009) tested the ferric loaded resin anion exchanger D-201 by treating a synthetic solution with a concentration of 10-1000 mg L⁻¹ phosphate, obtaining a capacity of 17.8 mg gmedia⁻¹. Other authors such as O'Neal & Boyer (2013) tested PhosXnp or LayneRT-commercially available ferric loaded anion exchange resin and treated a synthetic urine solution with a concentration of 20 mmol L⁻¹ phosphate and 10-900 mmol L⁻¹ sulphate, obtaining a capacity of 10.1 mg gmedia⁻¹.

Table 3 shows different ion exchange resins loaded with different metal oxides that have been studied.

Table 3. Different sorbents loaded with metal oxides.

Material	Source of water	Water composition	Outcomes	Reference
PhosXnp or LayneRT – commercially available ferric loaded anion exchange resin	Synthetic urine	PO ₄ ⁻³ (20 mmol L ⁻¹) SO ₄ ²⁻ (15 - 30 mmol L ⁻¹)	Capacity: 9.54 mg gmedia ⁻¹	Sendrowski and Boyer, 2013
Purolite FerrIX A33E – commercially available iron oxide loaded anion exchange resin	Synthetic	PO ₄ ⁻³ (5-30 mmol L ⁻¹)	Capacity: 48 mg gmedia ⁻¹	Nur et al., 2014
Ferric oxide loaded IRA-400 (Amberlite)	Synthetic	PO ₄ ⁻³ (5mg L ⁻¹)	Capacity: 111.1 mg gmedia ⁻¹	Acelas et al., 2015
Copper oxide loaded IRA-400 (Amberlite)	Synthetic	PO ₄ ⁻³ (5mg L ⁻¹)	Capacity: 74.07 mg gmedia ⁻¹	Acelas et al., 2015
Purolite FerrIX A33E – commercially available iron oxide loaded anion exchange resin)	Synthetic	PO ₄ ⁻³ (20mg L ⁻¹)	Saturation: 3-28 hours	Nur et al., 2014
LayneRT – commercially available iron oxide loaded anion exchange resin	Groundwater	PO ₄ ⁻³ (4 mg L ⁻¹) SO ₄ ²⁻ (204 mg L ⁻¹)	Saturation: 830 BV	Martin et al., 2013

Despite many studies have tested different metal oxides and resins, the one with the best results is a selective phosphate sorbent, called hybrid anion exchanger or HAIX. As explained above, hydrated Fe

(III) oxide or HFO is a harmless, inexpensive, readily available, and chemically stable material over a wide pH range. A study by Cumbal & Sengupta, (2005) has shown that the sorption capacity of the ligand can be increased by dispersing HFO nanoparticles within polymeric anion exchangers. This is due to the Donnan membrane effect exerted by the fixed positive charges of an anion exchanger.

The method for dispersing HFO nanoparticles in an anion exchanger is complex. However, there are economically viable techniques using environmentally friendly chemicals (Cumbal & SenGupta, 2005).

Figure 4 shows a schematic of a HAIX bead in which HFO particles are dispersed within an anion exchanger containing quaternary ammonium functional groups (R_4N^+).

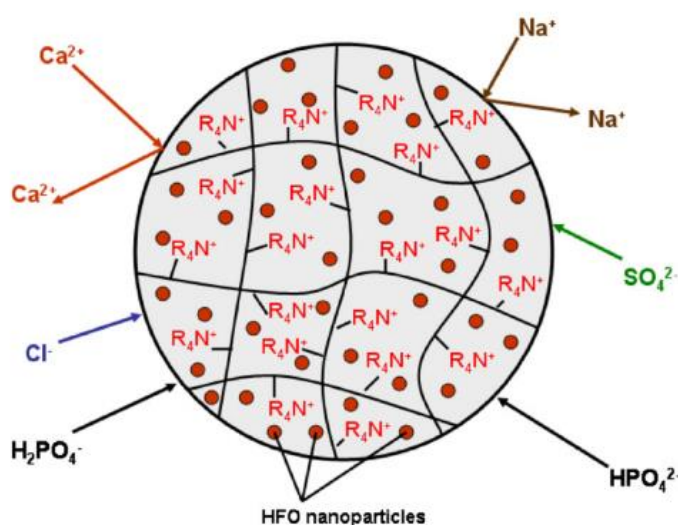


Figure 4. Representation of an HAIX resin with quaternary ammonium functional groups (R_4N^+) irreversibly dispersed with HFO nanoparticles. (Blaney et al., 2007)

A study by Blaney et al. (2007) compares two different sorbents, the IRA-900 and the HAIX. It is observed that for the IRA-900, phosphate breakthrough occurs at less than 200 BV while the HAIX was able to continue operating after 2000 BV. Furthermore, the authors conclude that HAIX offers a high selectivity towards phosphate in the presence of other anions. Another study by Guida et al. (2021) studied phosphorus removal from wastewater using HAIX, achieving an average removal of $6 \text{ mg PO}_4\text{-P L}^{-1}$, with a resin capacity of $4.1 \text{ mg PO}_4\text{-P gresin}^{-1}$.

In summary, media loaded with metal oxides have been shown to be effective in phosphorus removal achieving concentrations below 0.1 mg P L^{-1} in synthetic waters and real effluents. However, such media have some limitations such as excessive pressure drops due to solids accumulation. Therefore, metal oxide media are more suitable for tertiary treatment, after settling tanks.

3.2.3. Regeneration of hybrid anion exchange resins

The regeneration process of HAIX resins involves the removal of phosphorus ions that have accumulated in the resin during the adsorption process. This operation is a key part of any ion exchange process and must be carried out as efficiently and economically as possible. An alkaline solution can be used to deprotonate the HFO nanoparticles, while the polymeric structure can be regenerated with brine (e.g., NaCl) like the usual ion exchange processes (Muhammad, 2019).

During regeneration of the resin, more than 90% of the $\text{PO}_4\text{-P}$ adsorbed on the regenerant solution can be concentrated by reusing the same regenerant solution several times. In addition, the reuse of regenerant contributes to reducing the environmental impact of the process by reducing the amount of chemicals needed for the operation (Guida et al., 2021).

Table 4 shows different types of regeneration solution as well as the regeneration efficiency for HAIX that has been carried out in different studies.

Table 4. Regenerant solutions used for HAIX.

Treated solution	Water composition	Regeneration efficiency	Reference
Sludge liquor, municipal WW	$\text{PO}_4\text{-P}$ (350 mg L ⁻¹)	95% (1 M NaOH)	Bottini & Rizzo, 2012
Real and synthetic WW	$\text{PO}_4\text{-P}$ (4.8 mg L ⁻¹)	88% (2-5% NaCl and 2-5% NaOH)	Martin et al., 2018
Municipal WW	$\text{PO}_4\text{-P}$ (4 mg L ⁻¹)	N/A (NaCl-NaOH)	Marin et al., 2013
Secondary WW effluent	$\text{PO}_4\text{-P}$ (100 mg L ⁻¹)	90% (4% NaOH)	Muhammad, 2019
Synthetic solution	$\text{PO}_4\text{-P}$ (5 mg L ⁻¹)	>90% (2% NaCl and 2% NaOH)	Acelas et al., 2015
Organic-rich surface water	$\text{PO}_4\text{-P}$ (132-250 μ L ⁻¹)	80% (NaCl-NaOH)	Boyer et al., 2011

As can be seen, a mixture of NaOH and NaCl is usually used as the regenerant solution. However, the highest efficiency (95%) was obtained with a 1M NaOH solution.

Subsequently, the saturated regenerant solution can be processed to recover phosphorus in the form of fertilizer. For example, crystallization in the form of struvite has been extensively studied although the regenerant solution does not contain magnesium. Depending on the operational conditions, different forms of calcium phosphate such as hydroxyapatite, octa calcium phosphate, tricalcium phosphate, monoteite or brushite can be obtained. The recovery efficiency will largely depend on the initial phosphorus concentration (Ansari et al., 2016; Guida et al., 2021).

4. Base scenario

The conventional process for the biological removal of nitrogen and chemical removal of phosphorus from wastewater is shown in Figure 5. The process is characterised by the recycling of nitrified liquor containing nitrite and nitrate at the end of the aerobic zone to the anoxic zone for denitrification. In the anoxic zone, denitrifying microorganisms break down nitrates to nitrogen gas while in the aerobic zone ammoniacal nitrogen is oxidised into nitrates and nitrites by the action of aerobic microorganisms. Subsequently, the active sludge is sent to the secondary settling tank where FeCl_3 is added to precipitate and remove the phosphates present in the wastewater. However, although this conventional process is widely used in wastewater treatment, it has some limitations, such as high sludge production, inefficiency in the removal of some pollutants and high aeration costs (Deng *et al.*, 2014; Park & Dho, 2018).

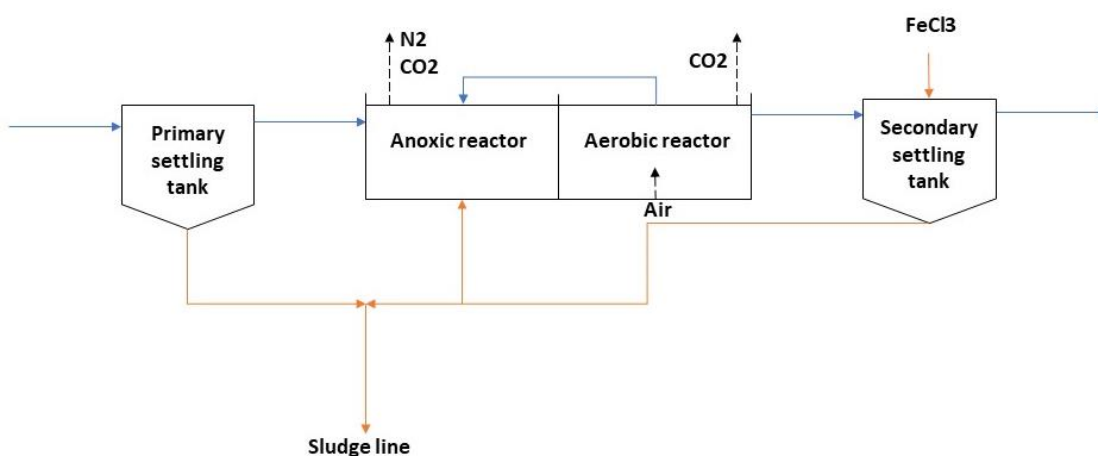


Figure 5. Conventional process for biological removal of nitrogen and chemical removal of phosphorus.

Due to the disadvantages of the conventional process, it is necessary to look for alternative technologies that are able to reduce aeration and sludge disposal costs and recover valuable products, contributing to the circularity of the process. The anaerobic membrane bioreactor (AnMBR) is presented as an alternative that is capable of producing a high-quality effluent, with no suspended solids and 95-99% chemical oxygen demand (COD) removal (Saddoud *et al.*, 2007; Lin *et al.*, 2009). In this process, the organic matter contained in the municipal wastewater is oxidised into biogas (methane content 60-70%) while the sludge is retained into the system by using a membrane separation system (Vinardell *et al.*, 2020). Subsequently, the biogas can be burned to generate heat or electricity, making it a sustainable alternative (Skouteris *et al.*, 2012).

The AnMBR process has advantages in economic terms as no aeration is needed, methane is recovered, sludge production is very low compared to the conventional process and the quality of the treated water is high (Deng et al., 2014). However, this technology faces several challenges such as membrane fouling, dissolved methane, and nutrient control (Liao et al., 2006; Kim et al., 2011; Kim et al., 2002).

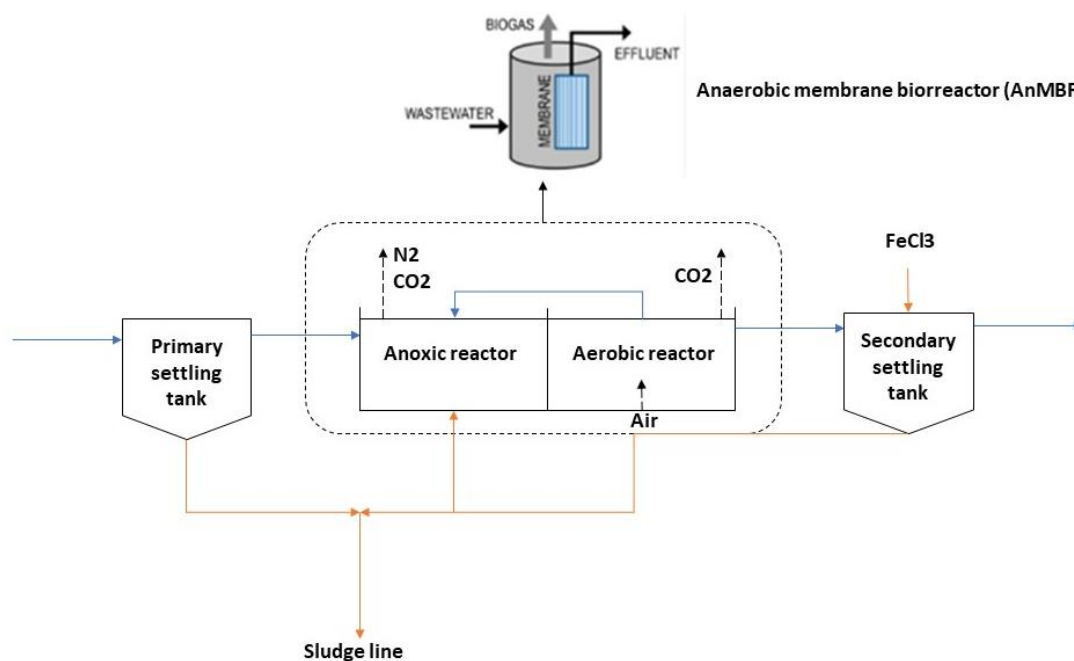


Figure 6. The Anaerobic MBR as an alternative to conventional wastewater treatment.

Phosphorus could be removed with coagulants, but nitrogen removal is more challenging. If biological nitrogen removal is desired after the AnMBR operation, the costs will increase due to the amount of air to be supplied for nitrification and the significant amounts of exogenous electron donor for denitrification. Therefore, physical, or chemical methods are more appropriate for nutrient removal from the AnMBR effluent (Huang et al., 2020).

Ion exchange technologies are complementary to the characteristics of the AnMBR permeate (no suspended solids and low COD). For example, Deng et al. (2014) stated that organic nitrogen is hydrolysed to ammonium nitrogen in AnMBR permeates, which is ideal for ion exchange of natural zeolite. In addition, the permeate does not contain any particulate matter, so clogging in the ion exchange columns is significantly reduced. Huang et al. (2020) compared the AnMBR+IEX with (conventional activated sludge process) CAS+IEX configurations, concluding that the AnMBR configuration provides an effluent without suspended solids, improving the efficiency of adsorption and stability of the IEX process.

In addition, the AnMBR configuration presents another advantage with respect to nutrient recovery, since it provides an effluent with a higher concentration of nutrients than conventional water treatment processes, which further facilitates nutrient recovery through ion exchange technologies. This technology is also capable of considerably reducing direct greenhouse gas emissions and allows both energy and nutrient recovery, which is in line with the circular economy vision (Guida *et al.*, 2021).

In summary, the combination of AnMBR with ion exchange processes is a promising strategy for the selective recovery of nutrients from wastewater. For this reason, the recovery of nitrogen and phosphorus from the effluent of an AnMBR will be the basis of the work for the evaluation of ion exchange technologies to recover nitrogen and phosphorus from municipal wastewater.

Finally, it is important to note that the selective recovery of nitrogen (N) and phosphorus (P) by ion exchange technologies can be applied to other types of effluent, such as effluents from aerobic activated sludge processes.

5. Methodology, description of the case study and design parameters

The case study considered in this work for the techno-economic evaluation of ion exchange technologies is based on an operating capacity of 20000 m³ day⁻¹ of municipal wastewater with a concentration of 56 mg L⁻¹ NH₄-N and 14 mg L⁻¹ PO₄-P (Vinardell et al., 2021). As explained in the previous section, the wastewater comes from the permeate of an AnMBR.

The treatment process includes specific ion exchange columns for the removal of each nutrient, followed by technologies for recovery of the nutrients in the form of fertiliser. Nitrogen fertiliser is recovered from the regenerant solution in the form of (NH₄)₂SO₄ using liquid-liquid membrane contactor (LLMC) technology, while phosphate fertiliser is recovered from the regenerant solution in the form of hydroxyapatite Ca₅(PO₄)₃OH(s) using precipitation technologies. After these stages, the regenerant solution is recycled to the process to reduce the overall consumption of chemicals.

The flow diagram of the proposed process is shown in the following figure:

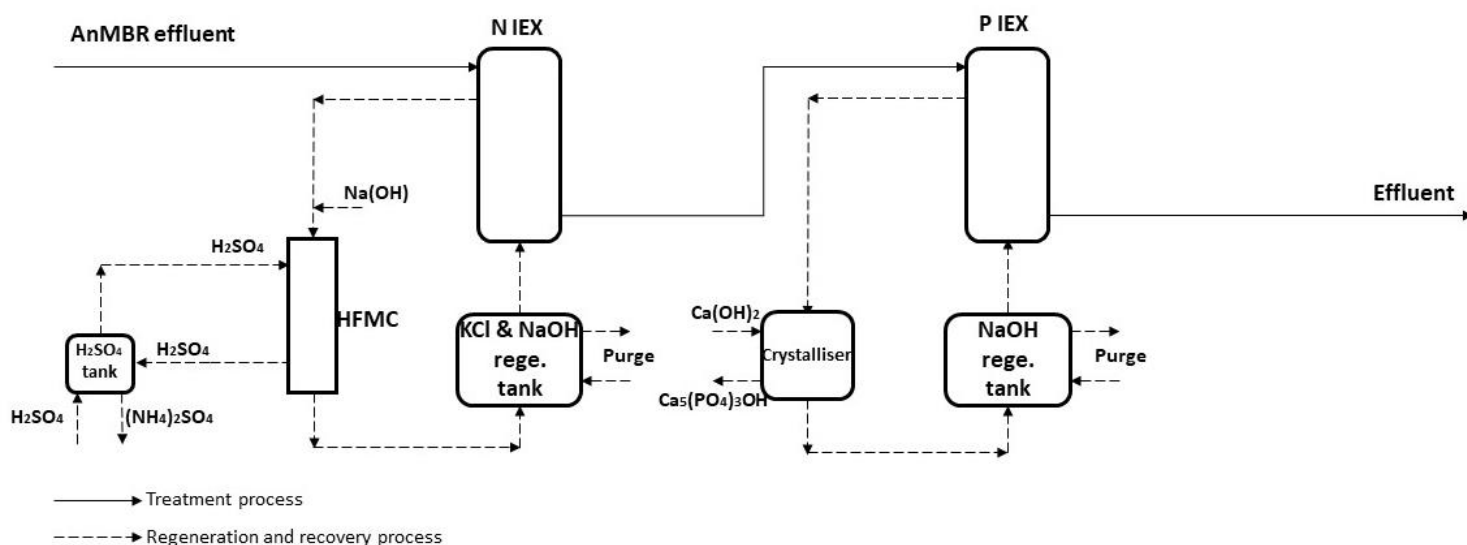


Figure 7. Flow diagram of the municipal wastewater treatment plant for nutrient recovery.

The wastewater treatment plant operates 320 days a year, 24 hours a day, with the remaining days reserved for maintenance. Regarding the mode of operation, the wastewater passes through fixed bed resin columns until saturation is reached. Subsequently, the resin is regenerated, while another system of columns is used to provide continuous treatment. Because of this process, the ion exchange columns are operated in parallel to continue operation when regeneration of the resins is needed.

For regeneration, the counter-current mode is used, where the regenerant (upward direction) passes through the resin in the opposite direction to the wastewater being treated (Crittenden et al., 2012). Counter-current operation has been selected as it will result in lower leakage levels and higher chemical efficiencies than co-current operation. In addition, this mode of operation should be used in situations where high purity water is required and chemical consumption should be optimised (Crittenden et al., 2012).

5.1. Design parameters

This section will present the main design parameters of the nutrient recovery processes as well as the assumptions that have been made in each part of the process. These parameters are essential to ensure the correct operation of the plant and to obtain the desired results in terms of removal efficiency and recovery. The plant design has been calculated based on data obtained from different scientific studies and manufacturers' specifications. The formulas used and additional information for the design can be found in Annex A.

5.1.1. Fixed-bed ion exchange columns for ammonium removal and recovery

The design of the ion exchange columns for nitrogen removal was performed with different columns configured in parallel. In addition, a system of columns configured in parallel is also included to continue the operation of the system despite regeneration is needed for one of the systems. In this case, it has been assumed that the ion exchange columns are able to remove 93 % of the available ammonium from the water when MesoLite is used as resin (Canellas-Garriga, 2018).

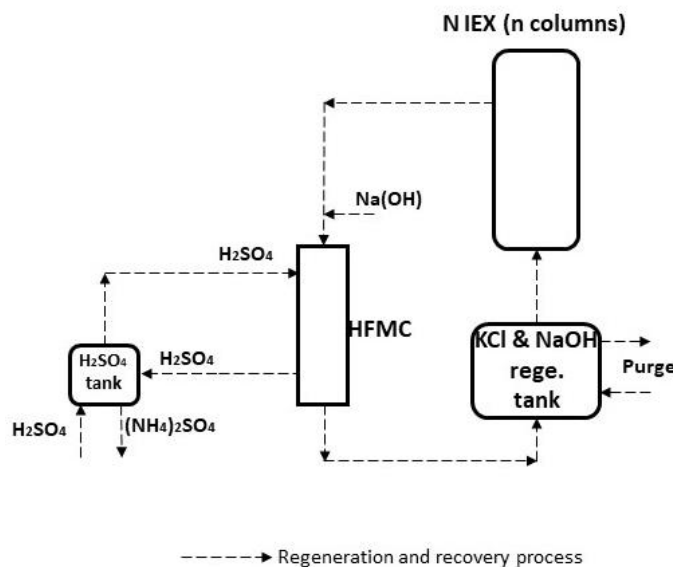


Figure 8. Flow diagram of the nitrogen recovery section.

The medium selected for ammonium removal is synthetic MesoLite as recent studies have shown that this zeolite has a high capacity for ammonium adsorption compared to other zeolites such as Clinoptilolite (Pabalan et al., 2001). The capacity of the MesoLite has been calculated by interpolating the values obtained from Thornton et al., (2007) as a function of the initial ammonium concentration in the wastewater and the empty bed contact time (EBCT).

Regarding the operation EBCT, a value of 10 min has been selected since this has been considered the EBCT that allows having an equilibrium between performance and cost for ammonium removal with MesoLite (Canellas-Garriga, 2018).

For the dimensioning of the individual columns, a maximum diameter of 3 m and a bed depth of between 0.75 and 3 m have been defined as these are values defined based on available literature (Towler & Sinnott, 2013; Crittenden et al., 2012). The maximum pressure drop in each column has been calculated based on the pressure drop graph (Annex A.2) of zeolite-61, assuming that the behaviour of zeolite-61 and MesoLite is similar.

The other design parameters have been calculated with the equations presented in Annex A.2.

A summary of the main design parameters of the ion exchange column for ammonium removal in the adsorption stage is shown in table 5.

Table 5. Design parameter for IEX process for ammonia removal (Adsorption stage).

Parameter	Unit	Value	Note	Reference
Adsorption stage				
Media		Mesolite		Mackinnon et al., 2003
Media capacity	g NH ₄ -N kg ⁻¹	7.6		Thornton et al., 2007
EBCT	min	10		Huang et al., 2020
Resin volume (BV)	m ³	138.9	Calculated	
Vessel diameter	m	3	Maximum diameter of 3 m	Towler & Sinnott. 2013
Bed depth	m	2	Industry range from 0.75 to 3 m	Crittenden et al., 2012
Total required surface area	m ²	69.4	Calculated	
Service area of one column	m ²	7.07	Calculated	
Required number of columns		10	Calculated	
Pressure drop	bar	0.11	Calculated	Zeolite-61
SFR	BV h ⁻¹	6	Calculated	
Breakthrough time	h	17.4	Calculated	

Breakthrough	BV	104.3	Calculated	
Packing density mesolite	kg m ⁻³	715		Canellas-Garriga, 2018
Permeate concentration	mg L ⁻¹	3.92	Calculated	
Media life	cycles	500	Trial with Clinoptilolite	Liberti et al., 1981

The design of the regeneration stage is important to ensure that the resin is properly regenerated, and that the column can be used in subsequent cycles efficiently.

Experimental results from Canellas-Garriga, (2018) indicated that regeneration efficiency increases with the pH. Therefore, the regenerant solution is based on a combination of 10% KCl and 2% NaOH (Deng et al., 2014; Canellas-Garriga, 2018). It was decided to use KCl as a regenerant because it has proven to be more effective than NaCl. In addition, KCl requires lower consumption than NaCl as 0.1 M KCl solution can achieve similar regeneration efficiencies than 1 M NaCl solution (Guida et al., 2019). Regarding the EBCT regeneration time, 1 hour has been assumed as several experimental studies show that this time is sufficient for resin regeneration (Huang et al., 2020).

The amount of regenerant required for each regeneration cycle has been determined by several literature studies using 5 BV to regenerate the MesoLite (Thornton et al., 2007; Huang et al., 2020). In terms of regeneration efficiency, it has been assumed that the resin is fully regenerated after the regeneration cycle.

Table 6 shows a summary of the main operating parameters for the regeneration of the MesoLite.

Table 6. Design parameter for IEX process for ammonia removal (Regeneration stage).

Parameter	Unit	Value	Note	Reference
<i>Regeneration stage</i>				
KCl concentration	%	10		Canellas-Garriga, 2018
NaOH concentration	%	2		Deng et al., 2014
EBCT regeneration	h	1		Huang et al., 2020
Regenerant required	BV	5		Thornton et al., 2007
Regenerations for each column	times/year	441.64	Calculated	
Regenerant tank volume	m ³	100	Calculated	
Number of tanks		7	Calculated	

5.1.2. Fixed-bed ion exchange columns for phosphate removal and recovery

As in the case of ammonium removal exchange columns, phosphate removal ion exchange columns operate in parallel. In addition, a system of columns configured in parallel is also included to continue the operation of the system despite regeneration is needed for one of the ion exchange systems. In

this case, it has been assumed that the ion exchange columns are capable of removing 95% of the phosphate present in the wastewater when HAIX is used as a resin (Guida et al., 2021).

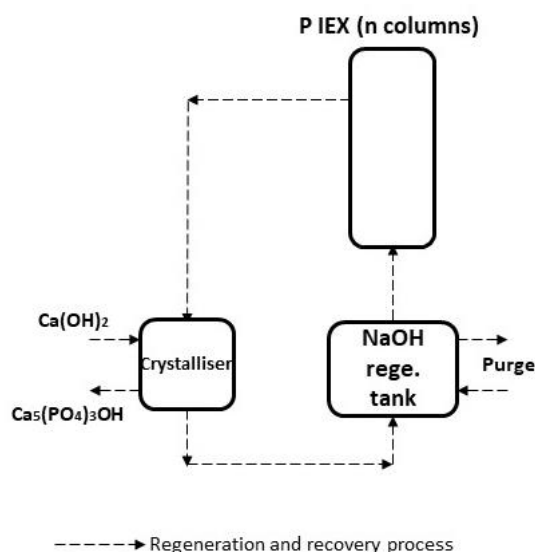


Figure 9. Flow diagram of the phosphorus recovery section.

The selected medium for phosphate removal is HAIX with ferric oxide nanoparticles embedded within the resin structure. This resin has been selected because of its high capacity in extended operating cycles. In addition, HAIX has proven to be more effective than other resins used for phosphate removal, such as Amberlite IRA-410 (Martin et al., 2009). Phosphate removal with HAIX is believed to be more efficient than removal by biological methods, especially when removal down to very low concentration levels is desired (Huang et al., 2020).

For EBCT, a value of 5 minutes has been selected as this value has been used by several studies (Muhammad et al., 2019; Huang et al., 2020).

For the dimensioning of the individual columns, a maximum diameter of 3 m and a bed depth of between 0.75 and 3 m have been defined based on available literature (Towler & Sinnott, 2013; Crittenden et al., 2012). The maximum pressure drop in each column has been calculated based on the pressure drop graph (Annex A.2) of HAIX ASM-125, assuming that the behaviour of HAIX ASM-125 and HAIX with ferric oxide nanoparticles embedded is similar.

The other design parameters have been calculated with the equations presented in Annex A.2.

A summary of the main design parameters of the ion exchange column for phosphate removal in the sorption stage is shown in table 7.

Table 7. Design parameter for IEX process for phosphate removal (Adsorption stage).

Parameter	Unit	Value	Note	Reference
Adsorption stage				
Media		HAIX with ferric oxide nanoparticles embedded		Pinelli et al., 2022
Media capacity	g PO ₄ ⁻ P kg ⁻¹	4.1		Pinelli et al., 2022
EBCT	min	5		Muhammad et al., 2019
Resin volume (BV)	m ³	69.4	Calculated	
Vessel diameter	m	3	Maximum diameter of 3 m	Towler & Sinnott. 2013
Bed depth	m	2	Industry range from 0.75 to 3 m	Crittenden et al., 2012
Total required surface area	m ²	34.72	Calculated	
Service area of one column	m ²	7.07	Calculated	
Required number of columns		5	Calculated	
Pressure drop	bar	0.33	Calculated	ASM-125
SFR	BV h ⁻¹	12	Calculated	
Breakthrough time	h	25.7	Calculated	
Breakthrough	BV	308.2	Calculated	
Packing density mesolite	kg m ⁻³	1,000		Muhammad et al., 2019
Permeate concentration	mg L ⁻¹	0.7	Calculated	
Media life	cycles	600		Muhammad et al., 2019

Regarding the regeneration stage, 10 BV of a 4% NaOH solution with an EBCT of 20 minutes was used based on data provided by different studies (Pinelli et al., 2022; Muhammad et al., 2019; Martin et al., 2009). In terms of regeneration efficiency, it has been assumed that using an excess of regenerant of 10 BV gives an efficiency of 100%.

Table 8 shows a summary of the main operating parameters for the regeneration of the HAIX.

Table 8. Design parameter for IEX process for phosphate removal (Regeneration stage).

Parameter	Unit	Value	Note	Reference
Regeneration stage				
NaOH concentration	%	4		Martin et al., 2009

EBCT regeneration	h	0.33		Martin et al., 2009
Regenerant required	BV	10		Muhammad et al., 2019
Regenerations for each column	/year	299	Calculated	
Regenerant tank volume	m ³	100	Calculated	
Number of tanks		7	Calculated	

5.1.3. Liquid-liquid membrane contactor loop for nitrogen recovery and regenerant recycling

The recovery of nutrients from the regenerant is an essential step to obtain value-added products. The most promising solution considered by several studies is to clean and reuse the regenerant while recovering the nutrients.

Different technologies are available to recover ammonia in the form of ammonium sulphate, while obtaining a regenerant solution ready for recycling. Membrane technology is an alternative that is gaining special attention since it allows the removal of ammonia and its recovery from wastewater compared to other water treatment processes such as strippers, scrubbers, and deaeration systems. The liquid-liquid membrane contactor (LLMC) separation technique uses a membrane permeable to specific gaseous species contained in a liquid phase and captures them using a receiver liquid phase that chemically reacts with the gaseous species. The hydrophobic LLMC can be used as a medium to separate aqueous phases. The driving force for mass transfer of the species through the hollow fiber microporous membrane is the difference in concentrations between the two phases. Mass transfer stops when chemical equilibrium is reached (Ulbricht et al., 2013).

Since the system using Liqui-Cel membrane contactors technology has been successful on an industrial scale in the removal of ammonia and its recovery as fertiliser (Ulbricht et al., 2013), it has been decided to choose this same technology for the design of the regenerant recovery stage.

In order to remove ammonia from wastewater, it is necessary to convert NH_4^+ to free ammonia gas (NH_3). This is achieved by increasing the pH of the solution by adding an alkali (e.g. NaOH). The regenerant solution containing a high amount of free ammonia gas is fed to the Liqui-Cel extra-flow membrane contactor (3M™) via the shellside (Ulbricht et al., 2013). A countercurrent flow of an acidic solution is fed through the interior of the hollow fibers (lumenside). Due to the difference in ammonia gas concentrations between the two sides of the membrane, NH_3 gas is transferred across the microporous membrane. In the receiving phase, $\text{NH}_3(\text{v})$ reacts instantly with the acid to form an ammonium salt.

The rate of ammonia transfer is limited by the maximum flux that the membrane can operate and the gradient of concentrations from the inlet to the outlet of the module. Connecting membrane contactors in series is essential for optimal operation.

Prior to the design parameters of the operation, several assumptions have been made based on the literature. The amount of NaOH used to increase the pH of the regenerant solution has been calculated based on the assumption that the pH in the regenerant after the regeneration stage was lowered to pH 7, so it is necessary to achieve pH 10 to obtain free ammonia gas (Canellas-Garriga, 2018). The removal efficiency of NH₃ from brine has been assumed to be 90% (Canellas-Garriga, 2018; Ulbricht et al., 2013). For the reaction, it has been assumed that complete conversion of ammonia to ammonium sulphate is achieved.

Chemical consumption is the largest expense in a LLMC process. The benefit of ammonia removal and ammonium sulphate reuse must be balanced against the requirements for wastewater conditioning and maintenance of the chemical sorption process on the acid side. Acid consumption is dependent on the initial NH₃ concentration at the inlet: the more ammonia is transferred; the more acid is needed. The sulphuric acid will react instantly with the ammonia to form ammonium sulphate. For this reason, to maintain excess conditions and increase the absorption capacity, the acid stream was kept at pH<1.5 (Ulbricht et al., 2013).

The consumption of NaOH (50%) before starting the operation has been calculated to achieve a pH increase of the regenerant solution from pH 7 to pH 10, which is the appropriate pH to carry out the operation (Noriega-Hevia et al., 2021). To calculate the acid consumption, a solution of H₂SO₄ with an initial concentration of 0.1 M (Serra-Toro et al., 2022) has been taken, maintaining a ratio in excess compared to the amount of ammonia removed (pH<1.5). Once the acid leaves the membrane operation, it is recirculated to the acid tank and then fed back to the membrane. It is concluded by means of material balances that the acid can be recirculated for 11 cycles in which the excess conditions (pH<1.5) are still maintained. Subsequently, after the 11 cycles, the acid solution is replaced by a new one. Recirculation of the acid will maximise the use of acid and reduce chemical consumption.

The membrane design parameters as well as the pressure drop have been calculated from the equations in Annex A.3 and the manufacturer's specifications.

A summary of the main design parameters for the ammonia recovery and regenerant cleaning stage is given in Table 9.

Table 9. Design parameters for the recovery unit (LLMC) of N (Cleaning of regenerant (N) stage).

Parameter	Unit	Value	Note	Reference
<i>Cleaning of regenerant (N) stage</i>				
NH ₄ -N concentration in brine	mg L ⁻¹	1,086.80	Calculated	

Membrane type		Liquid-Cel extra flow 4x28-inch	Liqui-cel
Membrane area (1 module)	m ³	20	Liqui-cel
Membrane area required	m ²	3,773	Calculated
Number of modules		189	Calculated
Total flow rate of regenerant	m ³ h ⁻¹	37.76	Calculated
Total flow rate of acid	m ³ h ⁻¹	1.07	Calculated
Pressure drop	bar	0.76	Calculated
Brine volume	m ³	694.44	Calculated
Cycle	h	18.39	Calculated
Time to replace the acid solution	cycles	11	Calculated
NaOH (50% required)	m ³ cycle ⁻¹	0.0056	Calculated
H ₂ SO ₄ (0,1 M) required	ton	20.46	Every 11 cycles
(NH ₄) ₂ SO ₄ formed	ton	27.43	Every 11 cycles
Acid tank volume	m ³	21.64	Applying an oversizing of 10%

5.1.4. Hydroxyapatite recovery and regenerant recycling

It is considered that crystallisation processes can recover P from the liquid phase in the form of calcium phosphates which are similar to phosphate rocks.

Crystallisation in the form of calcium phosphate is a complex operation involving several parameters. It depends on the concentrations of calcium and phosphate ions, supersaturation, ionic strength, temperature, ion types and pH. There are different forms of crystallised calcium phosphate; Dicalcium phosphate dihydrate (DCPD), Dicalcium phosphate anhydrate (DCPA), Octocalcium phosphate (OCP), Tricalcium phosphate (TCP), Amorphous calcium phosphate (ACP) and Hydroxyapatite (HAP). The different specific forms obtained from calcium phosphate will depend mainly on pH and kinetics. The stable phase at pH 5 is dicalcium phosphate dihydrate (DCPD), octocalcium phosphate (OCP) at pH around 6 and hydroxyapatite (HAP) at pH 7 or above (Seckler et al., 1996; Desmidt et al., 2015).

In the particular case under study, phosphorus can be recovered in the form of calcium phosphate (hydroxyapatite) by adding hydrated lime to the spent NaOH regenerant resulting in the instantaneous formation of hydroxyapatite (Ca₅(PO₄)₃OH). The crystallisation of HAP is described by equation 5:



For the calculation of the design parameters, a conversion rate of 85% and a retention time for the reaction to take place of one hour have been assumed.

Regarding the chemical requirements, the amount of calcium hydroxide to carry out the reaction has been calculated considering a Ca:P ratio (mol/mol) of 2 (Huang et al.,2020). In this way, 0.4267 tonnes of hydroxyapatite are obtained per cycle.

The crystalliser volume has been calculated from the inlet volumetric flow rate of the compounds and the retention time.

The design parameters are summarised in table 10.

Table 10. Design parameters for the recovery unit of P (Cleaning of regenerant (P) stage).

Parameter	Unit	Value	Note	Reference
<i>Cleaning of regenerant (P) stage</i>				
PO ₄ -P concentration in brine	mg L ⁻¹	410	Calculated	
Total flow rate of regenerant	m ³ h ⁻¹	26.69	Calculated	
Brine volume	m ³	694.44	Calculated	
Cycle	h	26.02	Calculated	
Ca(OH) ₂ required	mol cycle ⁻¹	18,369.18	2 Ca:P ratio	Huang et al., 2020
Ca ₅ (PO ₄) ₃ OH precipitated	mol cycle ⁻¹	2,602.30	Calculated	
Ca ₅ (PO ₄) ₃ OH precipitated	ton cycle ⁻¹	1.31	Calculated	
Retention time	h	1	Assumed	
Crystalliser volume	m ³	29.38	Applying an oversizing of 10%	

6. Economic evaluation

The objective of this section is to explain the methodology used to carry out a detailed cost-benefit analysis of the project.

First, the capital costs (CAPEX) and the operation and maintenance costs (OPEX) of the project will be assessed. The purpose of this is to estimate the total costs of the project over the lifetime of the plant and to determine the cost per unit of nutrient recovered.

6.1. Costs estimation

CAPEX refers mainly to the investment in equipment and technology necessary for the construction and start-up of the plant and therefore, it is one of the key aspects in the economic evaluation of any project.

A common way to calculate CAPEX is using cost curves. These curves are based on historical data from industrial projects and allow estimating the costs of the required equipment and technologies based on the scale of the plant. From this data, the total investment cost for the construction of the plant can be estimated.

It is important to note that these cost curves are based on historical data and vary depending on the specific conditions of each project. Therefore, costs obtained in currencies other than the Euro (€) were converted at current exchange rates (2023). In addition, the historical cost data was updated to the current date by equation 6 (Ochs et al., 2023) using the average inflation in Spain from 2010 to 2023.

$$\text{Cost in year } A = \text{Cost in year } B * (1 + \text{Average inflation})^{\text{Year } A - \text{Year } B} \quad (\text{Eq. 6})$$

The coefficients of the cost curves used are given in table 11. The equipment is obtained on U.S. dollars, which is then converted into euros. The cost is obtained using the following equation (Towler & Sinnott, 2013):

$$C_e = a + b * S^n \quad (\text{Eq. 7})$$

Table 11. Purchased equipment cost for common plant equipment. (Towler & Sinnott, 2013)

Equipment	Unit for size, S	S lower	S upper	a	b	n	Reference
Tank	capacity, m ³	10	4,000	5,800	1,600	0.7	Towler & Sinnott, 2013
Pumps	flow L s ⁻¹	0.2	126	8,000	240	0.9	Towler & Sinnott, 2013

Where S is the size parameter, a and b are cost constants and n is the exponent.

On the other hand, the parameters for calculating the crystallizer price are given in table 12. The equipment price is calculated by the following equation (Diab & Gerogiorgis, 2017):

$$P_B = f * P_A * \left(\frac{S_B}{S_A}\right)^n \quad (\text{Eq. 8})$$

Table 12. Purchased equipment cost for common plant equipment. (Diab & Gerogiorgis, 2017)

Equipment	Capacity basis	ref cost, P _A (GBP)	ref capacity, S _A	f	n
Crystallizer	m ³	328,875	3	0.1033	0.53

Where P_A is the reference purchase price, n is the exponent depending on the equipment item, f is the factor used and S_A is the reference capacity.

6.2. Estimation of capital expenditures (CAPEX)

For the estimation of the CAPEX, the total equipment cost has first been calculated using cost curves and literature references. Subsequently, the total capital cost was calculated using typical capital cost factors based on delivered equipment costs. This calculation approach allows for greater accuracy and detail in the CAPEX estimation and provides a solid basis for the economic evaluation of the project.

Table 13 shows the costs of equipment for the plant. The costs have already been updated by using equation 6, using the average inflation rate in Spain from 2010 to 2023, which is 2.7 % (Jiménez, 2022).

Table 13. Cost of equipment for the wastewater treatment plant.

Ítem	Unit Cost	Unit	Notes	Reference	Number of ítems	Total cost
N IEX column	18,107	€ m ⁻¹	For contactors between 1 – 3 m diameter	Sinnot, 2005	20	1,536,080 €
P IEX column	3,917	€ m ⁻¹	For contactors between 1 – 3 m diameter	Muhammad et al 2019	10	166,171 €
Membrane	49	€ m ⁻²		Noriega-Hevia et al., 2021	1	261,458 €
Tank (acid recirculation)	From table 11		Cone roof tank	Towler & Sinnot, 2013	1	24,900 €
Regenerant solution tank (N)	From table 11		Cone roof tank	Towler & Sinnot, 2013	7	409,658 €
Regenerant solution tank (P)	From table 11		Cone roof tank	Towler & Sinnot, 2013	7	409,658 €
Crystallizer	From table 12			Diab & Gerogiorgis, 2017	1	181,896 €

MesoLite	1.48	€ L ⁻¹	Canellas-Garriga, 2018	20	591,656 €
HAIX	12.16	€ L ⁻¹	Muhammad et al 2019	10	2,430,590 €
WW circuit pumps	From table 11		Towler & Sinnott, 2013	2	113,764 €
N circuit pumps	From table 11		Towler & Sinnott, 2013	2	28,250 €
P circuit pumps	From table 11		Towler & Sinnott, 2013	2	26,739 €
LLMC circuit pumps	From table 11		Towler & Sinnott, 2013	2	22,849 €
Total					6,203,675 €

Once the total equipment cost for the wastewater treatment plant is obtained, other costs related to construction, design, engineering, and other indirect costs can be estimated for the total CAPEX estimation. The table 14 shows the typical factors (Smith, 2005) that have been used for the calculation of the capital cost based on delivered equipment costs as well as the results obtained.

Table 14. Typical factors for capital cost based on delivered equipment cost and results. (Smith, 2005)

Ítem	Factors for capital cost	Cost
Direct costs		
Equipment delivered cost	1	6,203,675 €
Installation of equipment	0.4	2,481,470 €
Piping	0.7	4,342,572 €
Instrumentation & controls	0.2	1,240,735 €
Electrical	0.1	620,367 €
Utilities	0.5	3,101,837 €
Off-sites	0.2	1,240,735 €
Buildings	0.2	1,240,735 €
Site preparation	0.1	620,367 €
Indirect costs		
Design, engineering and construction	1	6,203,675 €
Contingency	0.4	2,481,440 €
Total capital costs		29,777,642 €

Therefore, the total capital cost required to start the project is 29,777,642 €.

6.3. Estimation of operational expenditures (OPEX)

In this section an estimation of the OPEX associated with the operation and maintenance of the wastewater treatment plant has been carried out.

The OPEX estimation has first been made based on the chemical and energy requirements of the plant. In order to calculate the chemical costs, material balances have been carried out in the different processes of the plant, which has made it possible to estimate the amount of reagents required. On the other hand, for the calculation of energy costs, the following formulas were used to estimate the electricity consumption of each pump used in the plant:

$$g\Delta z + \frac{\Delta P}{\rho} - \frac{\Delta P_f}{\rho} - W = 0 \quad (\text{Eq. 9})$$

$$\text{Power} = (W * m) * \frac{100}{\eta} \quad (\text{Eq. 10})$$

Where; W is the work done by the fluid (J kg^{-1}), Δz is the difference in elevations (m), ρ is the liquid density (kg m^{-3}), ΔP is the difference of pressure between the tank and the column (N m^{-2}), ΔP_f is the pressure drop inside the equipment (N m^{-2}), Δz is the difference in hydrostatic head (m), m is the mass flow rate (Kg s^{-1}) and η is the pump efficiency (%). In this case, it has been assumed that the pumps have an efficiency of 75%.

The table 15 shows the chemical and electrical requirements of the treatment plant.

Table 15. Chemical and electrical requirements for the wastewater treatment plant.

ítem	Total electricity consumption	Unit
WW circuit pumps	10.53	kWh h ⁻¹
N circuit pumps	1.64	kWh h ⁻¹
P circuit pumps	0.30	kWh h ⁻¹
LLMC circuit pumps	0.01	kWh h ⁻¹
Chemical requirements		
KCl	2,309	ton year ⁻¹
NaOH	1,202	ton year ⁻¹
H ₂ SO ₄	776	ton year ⁻¹
Ca(OH) ₂	401	ton year ⁻¹
Water	33,619	m ³ year ⁻¹

Once the plant requirements have been obtained, the annual costs for each item have been calculated. The cost used has been selected from updated bibliographic sources. The total annual costs for each item are shown in table 16.

Table 16. Annual chemical and electrical costs.

Ítem	Cost	Unit	Note	Reference	Total cost
WW circuit pumps	0.2525	€ kwh ⁻¹	75% efficiency	Ec.europa.eu, 2023	20,419 €
N circuit pumps	0.2525	€ kwh ⁻¹	75% efficiency	Ec.europa.eu, 2023	3,183 €
P circuit pumps	0.2525	€ kwh ⁻¹	75% efficiency	Ec.europa.eu, 2023	576 €
LLMC circuit pumps	0.2525	€ kwh ⁻¹	75% efficiency	Ec.europa.eu, 2023	14 €
KCl	630.42	€ ton ⁻¹		Chemanalyst, 2023	1,456,181 €
NaOH	604.3	€ ton ⁻¹		Chemanalyst, 2023	726,757 €
H2SO4	219.75	€ ton ⁻¹		Chemanalyst, 2023	170,731 €
Ca(OH)₂	436.79	€ ton ⁻¹		Chemanalyst, 2023	175,228 €
H₂O	2	€ m ⁻³		Water News Europe, 2021	67,239 €

It has to be considered that chemical and electrical costs are variable. Therefore, fixed operating costs including maintenance and labour must also be considered. These costs have been calculated using typical factors taken from the literature (Sinnot, 2005; Huang et al., 2020; Vinardell et al., 2022). The operational and maintenance costs for the first year of operation are included in the following table:

Table 17. Annual production costs (OPEX).

Ítem	Typical values (%)	Cost (€/year)	Reference
Variable costs			
1. Raw materials	From mass balances	2,596,139 €	
2. Electricity	From energy balances	24,194 €	
Fixed costs			
3. Maintenance	2.5% of CAPEX	744,441 €	Huang et al., 2020
4. Operating labour	1% of CAPEX	297,776 €	Vinardell et al., 2022
5. Plant overheads	50% of ítem (4)	148,888 €	Sinnot, 2005
6. Supervision	20% of ítem (4)	59,555 €	Sinnot, 2005
7. Laboratory costs	20% of ítem (4)	59,555 €	Sinnot, 2005
Administrative costs			
8. Research and development	1% of direct production costs	39,305 €	Sinnot, 2005
Annual production cost		3,969,855 €	

The calculated OPEX is for the first year of operation. However, it is normal for operational costs to change each year due to the wear and tear of certain critical plant components and their need for replacement.

In this case, the ion exchange resins and membranes are critical components and must be replaced periodically to maintain the efficiency of the process. The frequency of resin replacement has been selected considering the average lifetime and the cycles that each resin operates annually. Thus, the MesoLite will be replaced every 2 years while the HAIX will be replaced every 4 years (Liberti et al., 1981; Muhammad et al., 2019). The membrane replacement cost was calculated assuming a membrane lifetime of 10 years.

It is important to take this factor into account when estimating the long-term operational costs. Finally, the following table shows all operational and maintenance costs expected over the 20-year life of the plant.

Table 18. Total OPEX for the 20-year lifetime of the plant.

Ítem	Cost
1. Raw materials (Regenerants, acid, lime, water)	51,922,789 €
2. Electricity	483,885 €
3. Maintenance	14,888,821 €
4. Operating labour	5,955,528 €
5. Plant overheads	2,977,764 €
6. Supervision	1,191,105 €
7. Laboratory costs	1,191,105 €
8. Research and development	786,110 €
9. Mesolite (change every 2 years)	5,324,911 €
10. HAIX (change every 4 years)	9,722,360 €
11. LLMC (change every 10 years)	261,458 €
Total	94,705,841 €

6.4. Fertiliser sales revenue

The estimation of the income to be generated from the sale of the fertilisers obtained from the nutrient recovery process is one of the key aspects of the economic evaluation.

As explained above, hydroxyapatite is a product with a high phosphorus content, which makes it ideal for use as a fertiliser. Ammonium sulphate, on the other hand, is a high quality, nitrogen-rich fertiliser that is widely used in agriculture.

The estimation of revenues from sales of these fertilisers is based on market prices that are as up to date as possible. However, it is important to note that these prices can vary depending on several factors. The revenues obtained from the sale of fertilisers are shown in table 19.

Table 19. Annual revenue from the sale of fertilisers.

Ítem	Recovered nutrients (ton year ⁻¹)	Price (€ ton ⁻¹)	Reference	Annual revenue
(NH ₄) ₂ SO ₄	1,041	530.60	MAPA España, 2023	552,471 €
Ca ₅ (PO ₄) ₃ OH(s)	385	270.00	Huang et al., 2020	104,160 €
Total				656,632 €

6.5. Life cycle cost calculation

The economic analysis of a project should also consider the financial impact over the lifetime of the project. This involves estimating recurring costs and incomes over time, as well as considering possible changes in economic conditions and costs associated with the maintenance and operation of the plant.

This subsection shows the methodology used to calculate the costs and incomes over the lifetime of the project. For this purpose, the initial capital costs (CAPEX) and the operating and maintenance costs (OPEX) have been considered. In addition, the incomes over the lifetime of the project have also been evaluated by focusing on the revenues generated by the sale of fertilisers obtained from the recovered nutrients.

Equations 11 and 12 were used to calculate the present value (PV) of the gross cost and revenue from fertiliser sales, respectively. Subsequently, the PV of the net cost was calculated as the difference between the PV of the gross cost and the PV of the sales revenue (Eq. 13) (Vinardell et al., 2022).

$$PV_{GC} = CAPEX + \sum_{t=1}^T \frac{OPEX_t}{(1+i)^t} \quad (\text{Eq. 11})$$

$$PV_{FR} = \sum_{t=1}^T \frac{FR_t}{(1+i)^t} \quad (\text{Eq. 12})$$

$$PV_{NC} = CAPEX + \sum_{t=1}^T \frac{OPEX_t - FR_t}{(1+i)^t} \quad (\text{Eq. 13})$$

Where PV_{GC} is the present value of the gross cost (€), PV_{FR} is the PV of the fertiliser revenue (€), PV_{NC} is the PV of the net cost (€), CAPEX is the capital expenditure (€), $OPEX_t$ is the operating expenditure at year t (€), FR_t is the fertiliser revenue at year t (€), i is the discount rate selected (5%) and T is the plant lifetime (20 years) (Vinardell et al., 2022).

7. Results and discussion

In this section, the results of the present work will be presented and discussed. The values obtained throughout the lifetime of the project will be analysed, as well as the specific contributions of each item to CAPEX and OPEX.

The general results obtained in the economic analysis of the project are presented in table 20. It is important to note that for a detailed year-by-year breakdown of values, it is recommended to consult Annex B attached in this report, which provides additional information on the distribution of income and expenditure flows over time.

Table 20. Present value (PV) of the gross cost, fertiliser revenue and net cost for the treatment plant.

PV gross cost	88,437,462 €
PV fertiliser revenue	8,183,095 €
PV net cost	80,254,366 €

The net cost obtained for the wastewater treatment and nutrient recovery is substantially higher than the revenues achieved from fertilizer commercialisation. This is understandable given that the main purpose of the plant is to remove nutrients from wastewater and not the generation of a direct income. It is also important to note that the investment required to establish and operate a quality, efficient and sustainable treatment plant is considerable, with CAPEX contributing approximately 37% of the net project cost.

The contribution of each type of equipment in relation to the total cost of the equipment purchased is illustrated in figure 10. This approach allows to evaluate and understand how the investment in different plant components is financially distributed and provides relevant information for decision making.

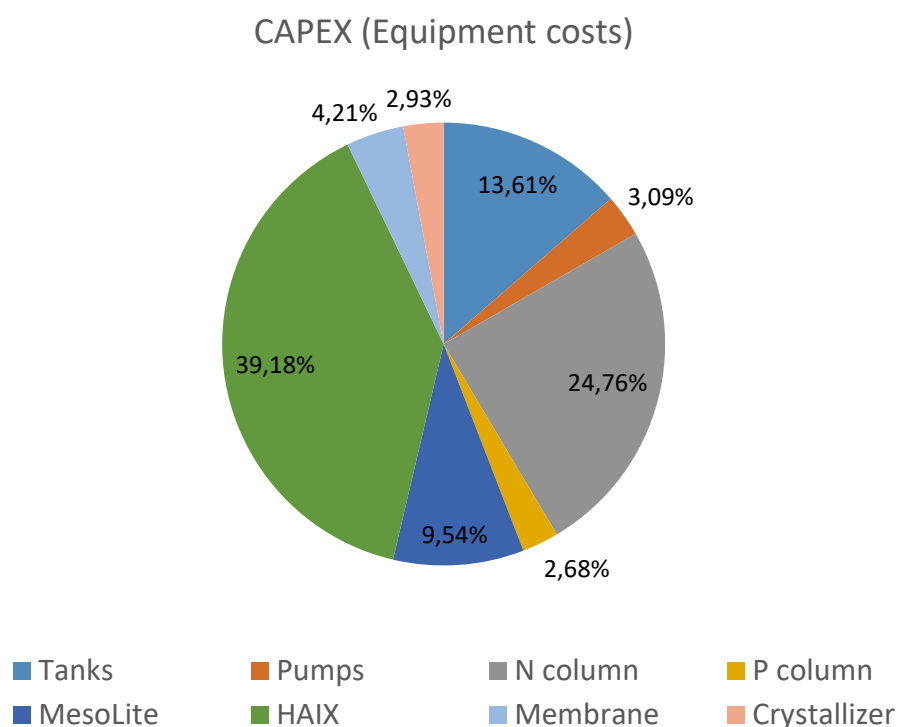


Figure 10. Breakdown of the contribution of each item to the total equipment cost.

In assessing the contribution of each type of equipment, the percentage of its cost compared to the total equipment cost has been calculated. The results show that the item that has the highest contribution in terms of cost compared to others is the hybrid anion exchange resin (HAIX) for phosphorus recovery, contributing 39.2% to the total equipment cost. The second largest contributing item (24.8%) is the ion exchange column for ammonium recovery (excluding the resin), followed by the tanks (13.6%) needed to store regenerants, acid and other plant chemicals. The MesoLite for ammonium recovery from wastewater also contributes considerably to the equipment cost (9.5%). However, its contribution is low compared to the ion exchange resin for phosphorus recovery.

Furthermore, a detailed breakdown of the different items contributing to OPEX over the 20-year lifetime of the plant has been carried out to identify and understand how operating costs are distributed over time (figure 11).

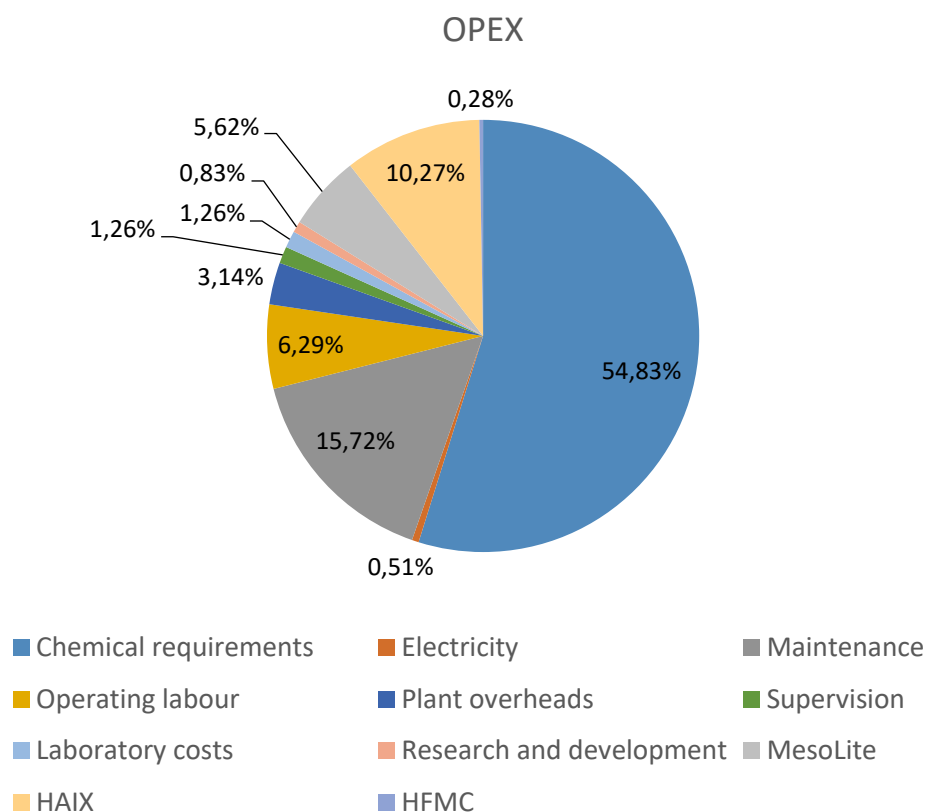


Figure 11. Breakdown of the contribution of each item to OPEX over the 20-year life of the plant.

The results reveal that the items contributing the most to the total OPEX, from highest to lowest, are:

1. **Chemical requirements:** Costs associated with the use of chemicals, such as regeneration agents or H_2SO_4 , represent more than half of the total OPEX (54.8%). It should be noted that the contribution of this item would be even higher if the reuse of regenerants were not included in the system.
2. **Maintenance:** Regular and preventive maintenance of the plant's equipment and systems is essential to ensure their optimal functioning. The costs associated with maintenance contribute 15.7% to the total OPEX.
3. **HAIX resin:** The ion exchange resin used for phosphorus recovery is a key component that has a noticeable impact on total OPEX (10.3%). The cost related to this item is based on its replacement every 4 years, as it is a component that over time can lose efficiency and must be replaced for the optimal operation of the plant.
4. **Operating labour:** Labour costs, including salaries of the operating and technical personnel involved in the operation and maintenance of the plant contribute 6.3 % to the total OPEX.

Finally, it has been determined that the replacement of the MesoLite (every two years) for ammonia recovery contributes 5.6% to the total OPEX. Other expenses such as supervision, laboratory, research and development costs and the ammonia recovery through LLMC contribute little to the total OPEX. It is worth noting that electricity costs make a low contribution to the total OPEX (0.5%), which leads to the conclusion that IEX processes consume relatively low electricity (Huang et al., 2020).

7.1. Nitrogen removal/recovery costs

In this section, the costs associated with nitrogen removal and recovery within the ion exchange system will be presented (figure 8). The main objective is to obtain an accurate estimate of the financial costs related exclusively to this part of the process, without considering the cost of phosphorus removal and recovery.

For the estimation of the costs for nitrogen removal and recovery, only those equipment and chemicals necessary for this stage of the process have been considered.

To assess the economic viability, a financial analysis was carried out which included the calculation of present values using equations 11, 12 and 13. The results obtained are shown in table 21.

Table 21. Present value (PV) of the gross cost, fertiliser revenue and net cost for the treatment plant (Nitrogen section).

PV gross cost	47,770,209 €
PV fertiliser revenue	6,885,021 €
PV net cost	40,885,187 €

According to the results obtained, the PV revenue for the nitrogen section represents 84% of the total plant revenue, so the nitrogen section contributes very significantly to the plant revenue. In relation to the PV net cost, it is concluded that the nitrogen section contributes 51%, so the net contribution of each section of the project is very balanced.

On the other hand, the total capital cost obtained for this part of the process is 14,072,333 € while the estimated production costs for the 20 years of plant operation is 54,264,562 €. Therefore, the capital cost (CAPEX) associated with the nitrogen removal and recovery part represents approximately 47% of the total capital cost of the plant, so the equal distribution of the capital cost between the removal and recovery parts of both nutrients is evident. On the other hand, this stage of the process contributes significantly to the overall operating costs of the plant (OPEX), accounting for approximately 57% of the total operating costs over the 20-year life of the plant.

The contribution of each piece of equipment to the total equipment cost of the nitrogen part has been identified in figure 12.

Distribution of equipment costs (N)

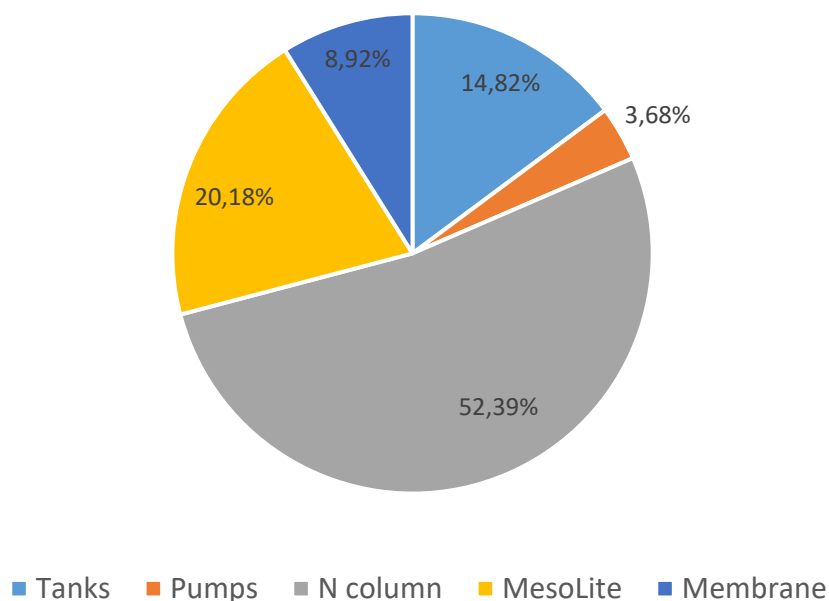


Figure 12. Breakdown of the contribution of each item to the total equipment cost (Nitrogen section).

The purchase of the ion exchange column is the item that features the highest contribution (52.4%) to the total equipment cost of the nitrogen removal and recovery part. The Mesolite is estimated to contribute 20.2% to the total equipment cost while the chemical storage tanks contribute 14.8%. Finally, the membrane and pumps are the items that contribute the least to this cost.

Regarding the operating costs over the 20-year lifetime of the plant, the contribution of each item is presented in figure 13.

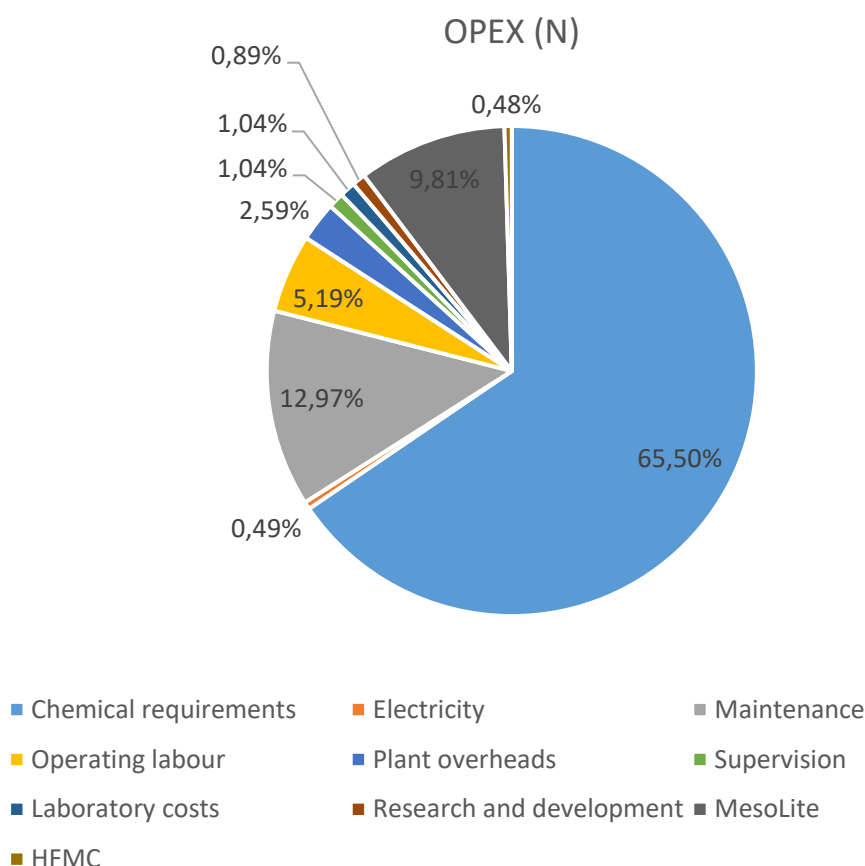


Figure 13. Breakdown of the contribution of each item to OPEX over the 20-year life of the plant (Nitrogen section).

As can be seen, chemical costs represent a very significant contribution, accounting for 65.5% of the total operating cost. Maintenance costs contribute 13% while Mesolite replacement to maintain system efficiency contributes 9.8%. The other elements and operating costs have been identified as minor contributions to the total operating cost of the nitrogen recovery process.

After a detailed analysis of the costs involved in nitrogen removal/recovery stage as well as the income obtained from the sale of the fertiliser, it has been determined that the net cost for nitrogen recovery is 6.81 € kg⁻¹ NH₄-N recovered. It is important to highlight that this value considers the total costs and considers the cash flow throughout the useful life of the project.

Nitrogen recovery prices can vary significantly depending on the technology used, the size of the plant, the operational parameters, and the treatment technology. However, to obtain a general perspective, the result obtained with other studies can be compared. An evaluation of ion exchange technologies for the recovery of nitrogen from wastewater in the form of (NH₄)₂SO₄ was carried out in the reference study by Huang et al, (2020). The cost obtained in this case was approximately 2.17 € kg⁻¹ NH₄-N recovered. Some differences that could explain these disparities in the results obtained are the scale

of the project, the mode of operation of the system, the efficiency and the treatment objective of each project, as well as economic factors. However, the difference can be considered relatively small, especially if one considers the general range of prices obtained in different studies and projects.

In another study carried out by Hao et al., (2017) it was estimated that the cost of recovering nitrogen with ion exchange technologies in the form of NH_4NO_3 was 1.83 € kg^{-1} $\text{NH}_4\text{-N}$ recovered, being a relatively low cost. Therefore, it must be considered that the difference in wastewater characteristics and in the final product can have a significant impact on the operating and capital costs. On the other hand, Lahav et al. (2013) concluded that the cost of recovering nitrogen (from swine wastewater) with ion exchange technologies varies in the range of 2-3 € kg^{-1} $\text{NH}_4\text{-N}$ recovered.

Regarding the industrial process of nitrogen synthesis through the Haber-Bosch process, a cost of approximately 0.28 to 0.7 € kg^{-1} N is obtained (Huang et al., 2020; Boulamanti & Moya, 2017), which is a much lower price compared to the result obtained in this study. These cost differences make direct competition between the two approaches difficult since large-scale industrial processes, such as the Haber-Bosch process, have been optimized for years to achieve the highest efficiency while minimizing costs. On the other hand, ion exchange technologies, while offering nutrient removal/recovery and environmental benefits, require significant upfront investments in specialized equipment and specific ion exchange resins. Furthermore, when comparing both approaches, it is important to note that industrial nitrogen production relies on economies of scale, whereas nitrogen recovery by ion exchange technologies is more suitable for projects where it is desired to treat wastewater to very low nitrogen concentrations and where the recovery of nutrients and reduction of environmental impact is valued, although this may involve additional costs.

Finally, the price obtained using ion exchange technologies is higher compared to conventional wastewater nitrogen removal processes, such as the nitrification-denitrification process, which generally has costs ranging between 2-4 € kg^{-1} N removed (Van Dongen et al., 2001). This is because the main objective of the conventional process lies in the removal of nitrogen from wastewater, while the ion exchange process implemented in this study aims to recover and obtain economic value from the nitrogen removed, which implies additional costs associated with the implementation of recovery technology (investment in ion exchange equipment, chemical products, operation, and maintenance, among others). Due to this fundamental difference in the objectives and approaches of the processes, it is expected that the cost obtained in this study will be higher in comparison with other conventional nitrogen removal processes. However, it is important to note that nitrogen recovery has additional benefits, such as obtaining a valuable product for use as a fertilizer and reducing dependency on external nitrogen sources.

7.2. Phosphorus removal/recovery costs

The aim of this section is to provide a detailed analysis of the economic aspects associated with phosphorus removal and recovery, without considering the nitrogen recovery part which was discussed in the previous section.

To assess the economic viability, a financial analysis was carried out which included the calculation of present values using equations 11, 12 and 13. The results obtained are shown in table 22.

Table 22. Present value (PV) of the gross cost, fertiliser revenue and net cost for the treatment plant (Phosphorous section).

PV gross cost	40,667,252 €
PV fertiliser revenue	1,298,073 €
PV net cost	39,369,179 €

The total net cost of the phosphorus section is 39,369,179 €, contributing 49% to the total project cost considering all sections. This implies that both phosphorus and nitrogen removal and recovery have a similar impact on the total project costs. Another important aspect is that the sale of phosphate fertiliser contributes only 16% of the total income from fertiliser sales. Therefore, although the sale of hydroxyapatite generates some revenue, it does not have a large benefit on the net cost of phosphorus removal stage.

On the other hand, the capital costs for this part of the process are 15,705,308 €, while the operating costs over the 20-year life of the plant are 40,441,278 €. These data reveal that the phosphorus part contributes approximately 53% to the total capital cost of the plant, while the contribution of operating costs to the total OPEX of the plant over the 20-year life of the plant is 43%.

The contribution of the different equipment to the total equipment cost of the phosphorous part is shown in figure 14.

Distribution of equipment costs (P)

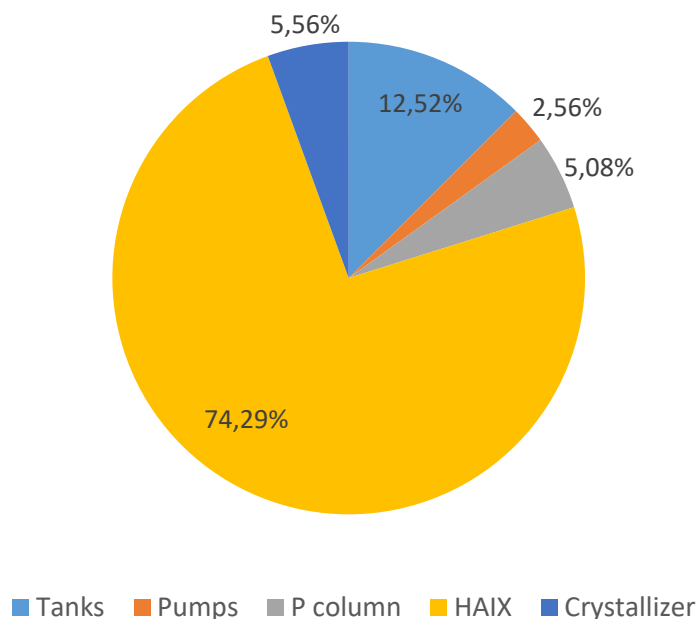


Figure 14. Breakdown of the contribution of each item to the total equipment cost (Phosphorous section).

As can be seen, the phosphorus ion exchange resin (HAIX) is the component that has the highest contribution to the total equipment cost (74.3%), followed by the tanks, the phosphorus ion exchange column, the crystalliser, and the pumps. This contribution reflects the importance of the HAIX and indicates that it is a critical element in the process in economic terms.

Regarding the operating costs over the 20-year lifetime of the plant, the contribution of each item is presented in figure 15.

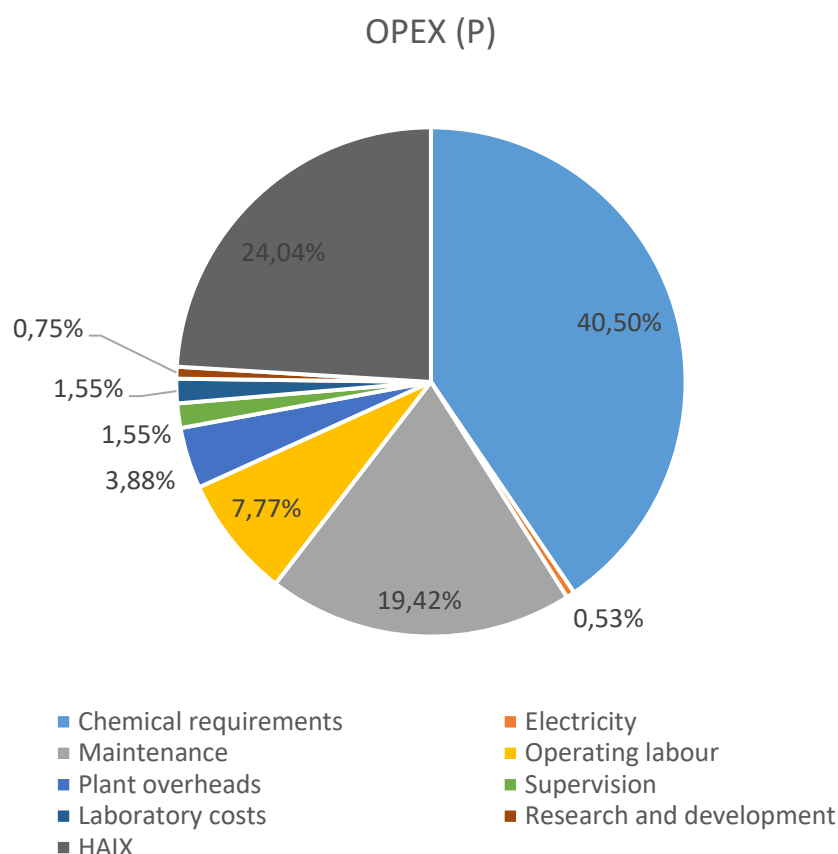


Figure 15. Breakdown of the contribution of each item to OPEX over the 20-year life of the plant (Phosphorous section).

Chemical requirements represent the largest expenditure contribution (40.5%) to total OPEX in the phosphorus train. This indicates that the use of chemicals is a relevant aspect in terms of operational costs, and it is important to optimise these resources as much as possible. Other items making a large contribution are ion exchange resin (HAIX) replacement (24%) and plant maintenance costs (19.42%).

After carrying out the detailed analysis on the phosphorus section, it has been determined that the cost for the phosphorus recovery is 27.21 €/kg PO₄-P recovered. It is important to highlight that the cost has been determined considering all the associated economic factors, including the income generated by the sale of the fertilizer.

The use of phosphate rock for fertiliser production is currently more cost-effective compared to the use of phosphate recovered by ion exchange technology. This is because the prices of raw phosphate rock and triple superphosphate are 0.6-1.2 € kg⁻¹ P and 1.2-2.2 € kg⁻¹ P (Desmidt et al., 2015) while the market price of struvite is 2.6 € kg⁻¹ P (Ashley et al, 2009). As expected, from a purely economic point of view, the strategy of using phosphate rock for fertiliser production is more economical than ion exchange technology for phosphorus recovery. However, it should be noted that the objective of this project is the removal of nutrients from wastewater, with the added value of their recovery in the form

of fertilisers. Furthermore, with the rising cost of conventional phosphate fertilisers (Muhammad, 2017) and the shift towards a more sustainable future, the need for technologies that can remove and recover phosphorus from wastewater is likely to increase.

The cost of conventional wastewater phosphorus recovery processes varies depending on the consumption of chemicals for the reaction and energy for mixing (Sakhivel et al., 2012). Using CaCl_2 and MgCl_2 as precipitators, the recovery costs (from the anaerobic digestion supernatant of sludge) are approximately 1.45-0.76 € kg^{-1} $\text{PO}_4\text{-P}$ respectively, while applying air stripping for increasing pH (Huang et al., 2015). However, when using NaOH solution to increase pH, the total costs while using CaCl_2 and MgCl_2 increase to 1.72-0.89 € kg^{-1} $\text{PO}_4\text{-P}$ (Ye et al., 2017). Furthermore, if MgO is used as a precipitating agent with air stripping, the price can decrease to 0.35 € kg^{-1} $\text{PO}_4\text{-P}$ (Ye et al., 2017). Comparing these traditional costs with the price obtained by using ion exchange technologies, there is a significant difference in economic terms. This difference may be due to several factors, for example that the water comes from different wastewater sources and contains different concentrations of phosphorus, that in some cases phosphorus is recovered from the sludge line, and that the ion exchange system requires a higher initial investment in terms of equipment and operations, which affects the final cost of the phosphorus recovered. In addition, the costs associated with the maintenance and regeneration of the ion exchange resins also play an important role in the final cost.

On the other hand, to get a broader perspective on these costs, the range of costs associated with phosphate removal during wastewater treatment has been considered. According to Dockhorn (2009), phosphate removal costs can range from 2 to 3 € kg^{-1} P as a minimum, up to more than 10 € kg^{-1} P under specific conditions. Furthermore, it has been observed that phosphate recovery costs can vary depending on the process used. According to Dockhorn (2009), these costs can be between 2.2 to 8.8 € kg^{-1} P, depending on the recovery method used. Another study by Egle et al. (2016) estimates the costs of P recovery from the liquid phase to be between 6 to 10 € kg^{-1} P recovered, while the total costs of recovery by wet chemical processes are between 9 and 16 € kg^{-1} P. These differences are due to the fact that the former process requires either converting the phosphate present in the sludge phase to the liquid phase by a wet chemical approach or increasing the bioavailability of the phosphate by thermochemical treatments. Again, it can be seen that phosphorus recovery costs are significantly affected by the characteristics of the wastewater or sludge being treated, the initial phosphorus concentration, the presence of other compounds and the recovery efficiency of the process.

Comparing these data with those obtained in the present study, it can be concluded that the ion exchange technologies used for P recovery have a higher cost relative to conventional removal and recovery costs. However, it is important to highlight that phosphorus recovery through ion exchange technologies offers additional benefits, such as obtaining a valuable product and contributing to the circular economy.

7.3. Sensitivity analysis

In this section of the report, a sensitivity analysis will be carried out to assess the impact of the main parameters, both operational and economic, on the total cost of the project. This analysis will make it possible to identify the most significant variables and understand their economic influence on the proposed system.

For each selected parameter, incremental and decremental variations in its values will be made, within a realistic range. This will provide a more complete picture of the uncertainty associated with the project and allow better decisions to be made on the key factors that may affect the economics of the project.

7.3.1. Operational parameters

In this section, sensitivity analysis of some key operational parameters will be carried out.

7.3.1.1. Empty bed contact time (EBCT)

The empty bed contact time (EBCT) refers to the average time the wastewater spends in contact with the ion exchange resins and is therefore a critical operational parameter in the system. The modification of this parameter has been done keeping the same treatment target and removal efficiencies as in the baseline case.

Several EBCT values have been considered (1, 2.5, 4, 8, 10 and 15 minutes), taking as reference the nitrogen column in the ion exchange process. In the case of the EBCT in the phosphorus column, the ratio established in the baseline case has been followed, which is 2:1 in relation to the EBCT of N columns. For example, when an EBCT of 8 minutes has been considered for the nitrogen ion exchange column, the EBCT for the phosphorus ion exchange column will be 4 minutes, according to the established ratio. This ensures operational consistency in the system.

It is important to note that the replacement time of the ion exchange resins has been kept constant in this analysis, following the same period established in the baseline scenario (replacement time of two years for Mesolite and four years for HAIX).

Figure 16 shows the results obtained for the different EBCT values and their impact on the capital cost. The results illustrate that the EBCT has a great influence on the equipment costs of the project. The trend observed is that the CAPEX increases as the EBCT value increases. For example, with an EBCT of 1 minute, the CAPEX stands at 6,709,622 €, while with an EBCT of 15 minutes, the CAPEX rises to 44,656,841 €. These results are explained by the fact that a change in EBCT implies a change in the

number of columns and ion exchange resins required to meet the treatment targets. With a smaller EBCT, less treatment capacity and therefore fewer columns and resins are required, which reduces equipment costs significantly. Conversely, larger EBCTs imply a larger capacity and thus a larger number of columns and resins, which increases equipment cost.

Furthermore, an analysis of the contribution of each piece of equipment to the total equipment cost shows that as the EBCT increases, the relative contribution of treatment equipment, such as resins and ion exchange columns, increases compared to other components of the system.

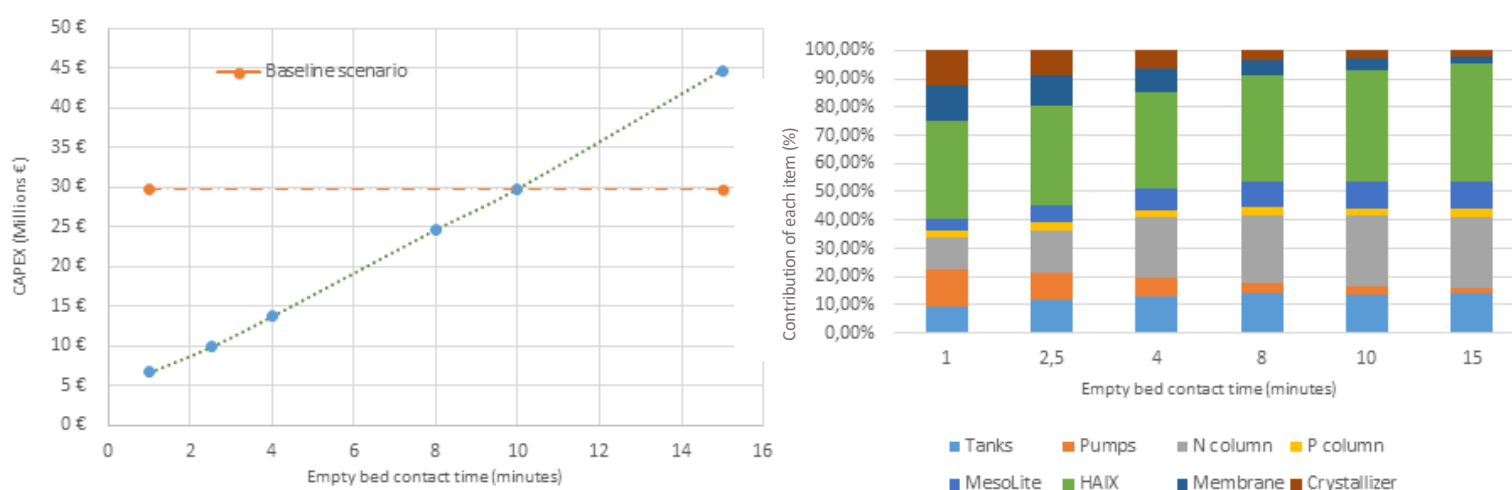


Figure 16. EBCT as a function of CAPEX (left) and contribution of each item to the total equipment cost for each EBCT (right).

Figure 17 shows the results obtained in relation to the EBCT and the total OPEX of the project over the 20-year lifetime of the project. When analysing the data, there is a clear correlation: as the EBCT value increases, the OPEX also increases. For example, with an EBCT of 1 minute, the OPEX stands at 46,888,403 €, while with an EBCT of 15 minutes, the OPEX rises to 117,659,590 €. The influence of EBCT on OPEX is explained by several factors. Firstly, as the EBCT increases, the amount of regenerant required for the regeneration of the ion exchange resins increases (because a larger volume of resin will have to be regenerated). Secondly, as discussed above, as the EBCT increases, the number of ion exchange resins that need to be replaced during the 20 years of operation also increases. Therefore, it is possible to conclude that the replacement of the ion exchange resins is a crucial factor in long-term operating costs.

In terms of the contribution of each item to total OPEX, a significant change is observed as EBCT varies. With small EBCT, chemical requirements are the item that contributes most to total OPEX. However, as the EBCT increases, the contribution of other items, such as maintenance costs, labour costs and resin costs, also increases. All these results are related to the increase in CAPEX as EBCT increases.

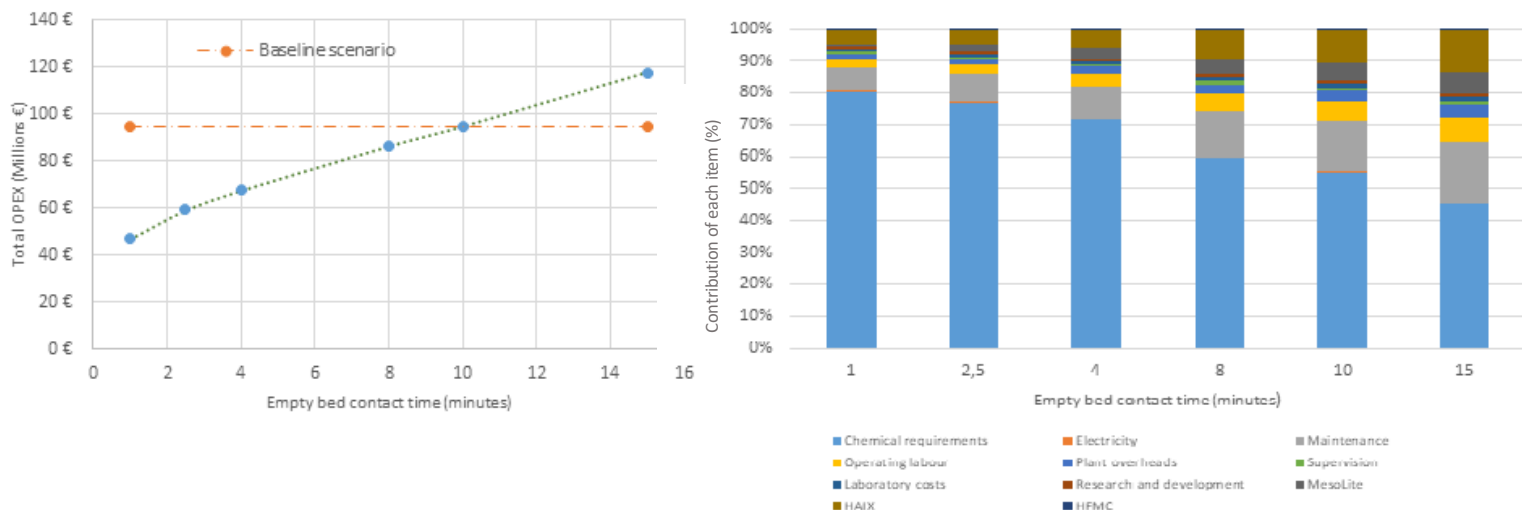


Figure 17. EBCT as a function of total OPEX (left) and contribution of each item to the total OPEX for each EBCT (right).

Figure 18 shows the results for the different EBCT values and their influence on the net cost of nutrient recovery. As expected, it is observed that as the EBCT increases, the cost of nutrient recovery also increases. For example, the recovery cost increases from 2.46 to 8.8 € kg⁻¹ NH₄-N as the EBCT increases from 1 to 15 minutes, respectively. In the case of PO₄-P, the recovery costs vary from 10.60 € kg⁻¹ with a 0.5 minutes EBCT to 38.92 € kg⁻¹ with a 7.5 minutes EBCT.

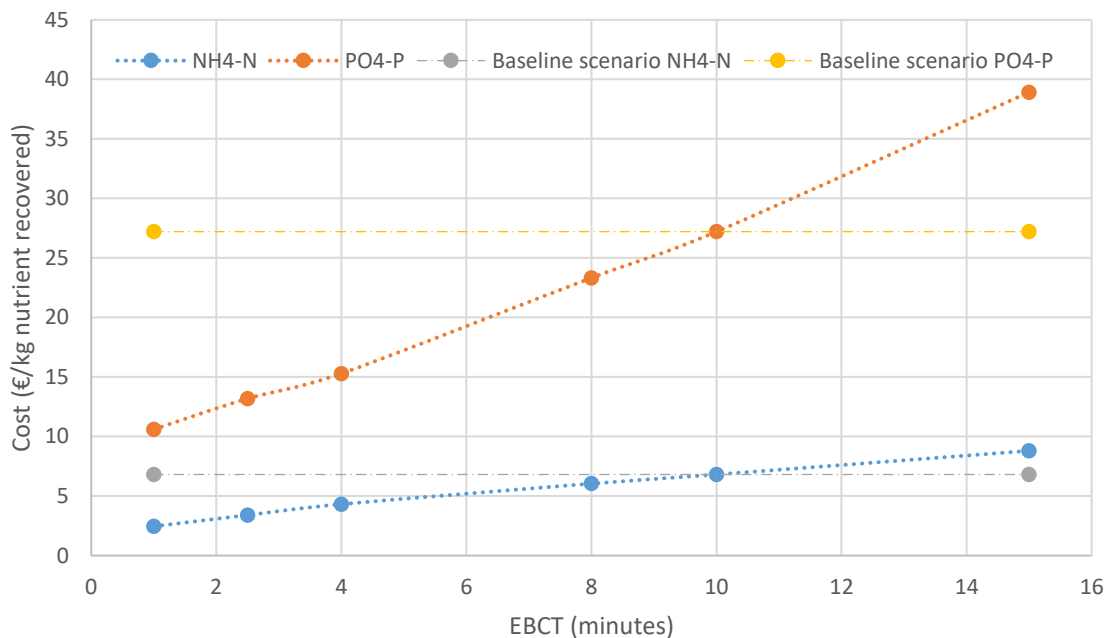


Figure 18. Variation in the recovery cost of each nutrient as a function of EBCT.

Figure 19 shows the impact of the different EBCTs on the total net cost of the project. It can be seen that the net cost of nitrogen recovery increases as the as the EBCT increases. For example, with an

EBCT of 1 minute, the total net cost is 30,074,975 €, while with an EBCT of 15 minutes, this cost rises to 109,108,522 €. The influence of the EBCT on the total net cost of the project is due to the factors discussed above; higher initial investment and operating costs as the EBCT increases.

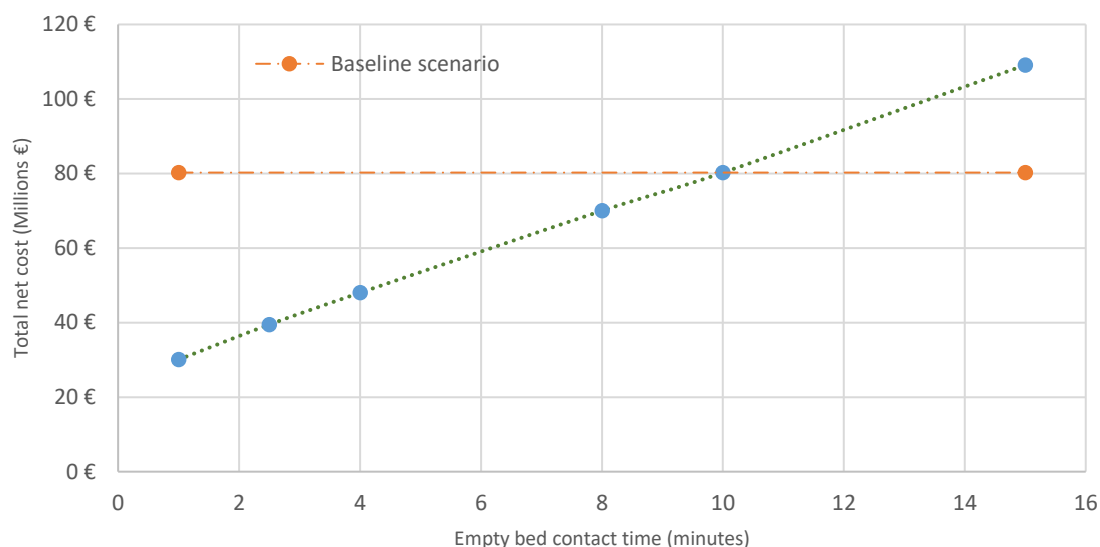


Figure 19. Total net cost of the project in function of the EBCT.

In conclusion, the sensitivity analysis carried out with different values of EBCT has provided an overview of the influence of this parameter on the total net cost of the project. The results show that EBCT plays a crucial role in the economics of the project, as it affects both the initial equipment costs and the operating costs over the lifetime of the plant. Therefore, it is important to find an optimal balance in the choice of EBCT and to carefully evaluate the costs and benefits associated with this parameter.

7.3.1.2. Ion exchange resin capacity and lifetime

The next operational parameter considered in the sensitivity analysis is the capacity of the resins (bed volumes to reach breakthrough). The impact of the lifetime of the ion exchange resins on the economic viability of the system has also been evaluated in this section. Both parameters are considered to be key parameters in the system as the resin capacity will determine the nutrient removal performance while the resin lifetime plays a key role in the replacement frequencies.

It should be noted that in this sensitivity analysis the objective is to maintain the same treatment capacity and disposal efficiencies as have been established in the baseline scenario. Moreover, the analysis has been carried out individually for each type of resin. In other words, when the capacity of the phosphorus resin (HAIX) has been modified, the capacity of the nitrogen resin (Mesolite) has remained unchanged with respect to the base case, and vice versa. This is because each type of resin has specific properties and characteristics that are not related to each other.

Figure 20 shows the results of the total net project cost as a function of the capacity of each resin. Regarding the MesoLite, it can be seen that when the resin capacity is reduced to approximately 40 BV to reach breakthrough, the total net cost increases by almost 8% compared to the base scenario, whereas if the resin capacity is increased to approximately 170 BV, the total net cost is reduced by 3.4% compared to the base scenario. On the other hand, with respect to HAIX, when the resin capacity is reduced to 150 BV, the total net cost rises by almost 10% while increasing the resin capacity to 600 BV reduces the total net cost by 4.2%.

Therefore, the direct relationship between resin capacity and the net cost of the project is evident. A change in resin capacity implies a change in the time required to reach breakthrough (less resin capacity, less time required to reach breakthrough). This change has an impact on the number of cycles the system performs, because as resin capacity decreases, more cycles will be required to maintain the desired removal efficiency. This, in turn, has a direct influence on the frequency of resin replacement, which has a significant impact on the net cost of the project.

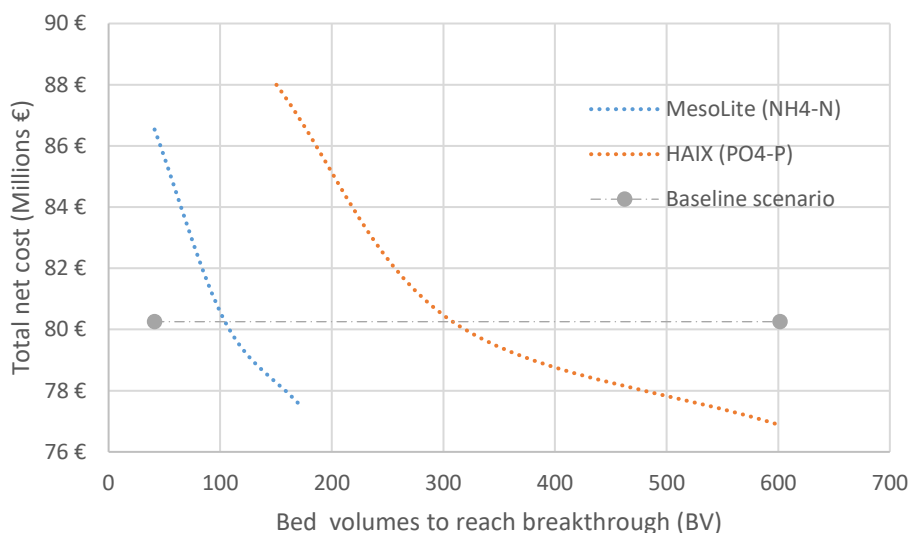


Figure 20. Total net cost of the project based on the capacity of each resin (bed volumes to reach breakthrough).

Figure 21 shows the different lifetimes of the resins as a function of the total net cost of the project. For MesoLite it is observed that when the lifetime is reduced to 250 cycles, the total net cost increases by 4.5% while if the lifetime is increased to 700 cycles, the total net cost decreases by 1.4%. With respect to HAIX, when the lifetime is reduced to 300 cycles, the total net cost increases by 9% while if the lifetime is increased to 900 cycles, the total net cost decreases by 2.3%.

These results are due to the fact that a change in resin lifetime implies a change in resin replacement frequency, which has a direct impact on the total net cost.

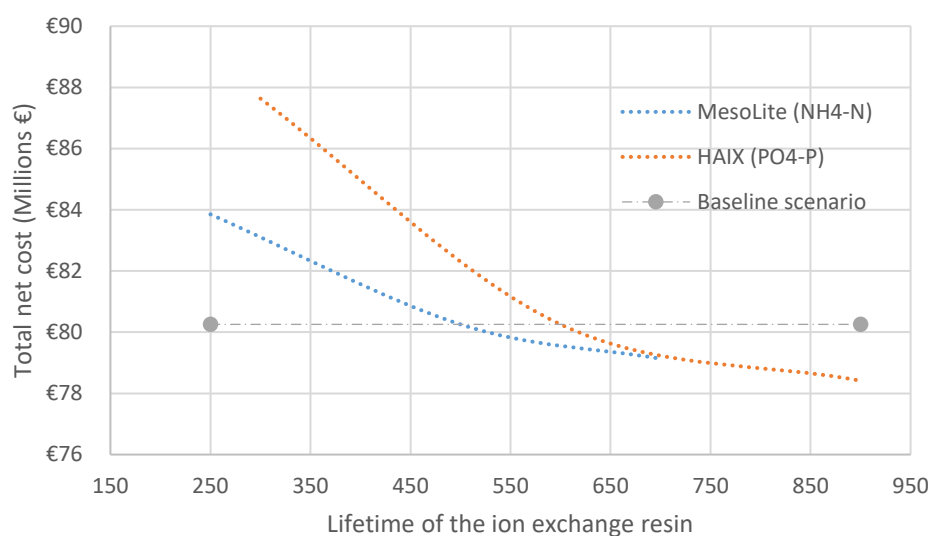


Figure 21. Total net cost of the project as a function of the lifetime of each resin.

In conclusion, it has been observed that there is an inverse relationship between the capacity and the frequency of resin replacement. In addition, there is also a trade-off between the capacity and the useful life of the resins, so that to increase the useful life of a resin, capacity must be sacrificed (Fakin et al., 2013). Taking the results obtained for the MesoLite and the HAIX as an example, it has been verified that increasing the capacity (maintaining the useful life of the resins), the total net cost can be reduced by 3.4 and 4.2%, respectively. However, by increasing the useful life of the resins (keeping capacity constant), a more limited total net cost reduction of 1.4 and 2.3% was obtained, respectively. These results show that the resin capacity features a higher influence than the resin lifetime on the net cost of the process, which suggest that it is important to increase the capacity of the resin (to offer longer cycles) at expenses of reducing its lifetime.

7.3.2. Economic parameters

The objective of this section is to assess how the considered economic parameters influence the total net cost of the project.

7.3.2.1. Change in the cost of phosphorus ion exchange resin (HAIX)

In this section, the impact of the change in the cost of the phosphorus ion exchange resin (HAIX) as a function of the empty bed contact time (EBCT) has been evaluated. The decision to perform this analysis is due to the fact that HAIX is the equipment that has the highest contribution to the total equipment cost of the plant. In addition, consideration was given to the fact that as the EBCT increases, the number of ion exchange resins required to meet the treatment objectives also increases.

Therefore, understanding how the change in the cost of this resin affects the initial project investment (CAPEX) is crucial.

In particular, a wide range of resin cost variation has been considered, from a 20% increase to an 80% decrease, including intermediate values.

The results obtained in the sensitivity analysis are shown in figure 22. The impact on the cost change of HAIX varies substantially depending on the EBCT, which is due to the importance of the EBCT in relation to the number of resins needed in the treatment system.

For example, when considering a 40% reduction in HAIX cost, it is observed that the total CAPEX decreases from 6,709,622 € to 5,776,276 € for an EBCT of 1 minute. In contrast, for an EBCT of 10 minutes, the total CAPEX decreased from 29,777,642 € to 25,110,909 €. These results further corroborate the importance of EBCT on the economics of the ion exchange system.

These results also illustrates that the differences in costs become more pronounced as the EBCT increases. This highlights the importance of finding the right balance in the system to reduce the negative impact that a change in resin cost can have on the CAPEX of the project without compromising the quality and efficiency of the treatment.

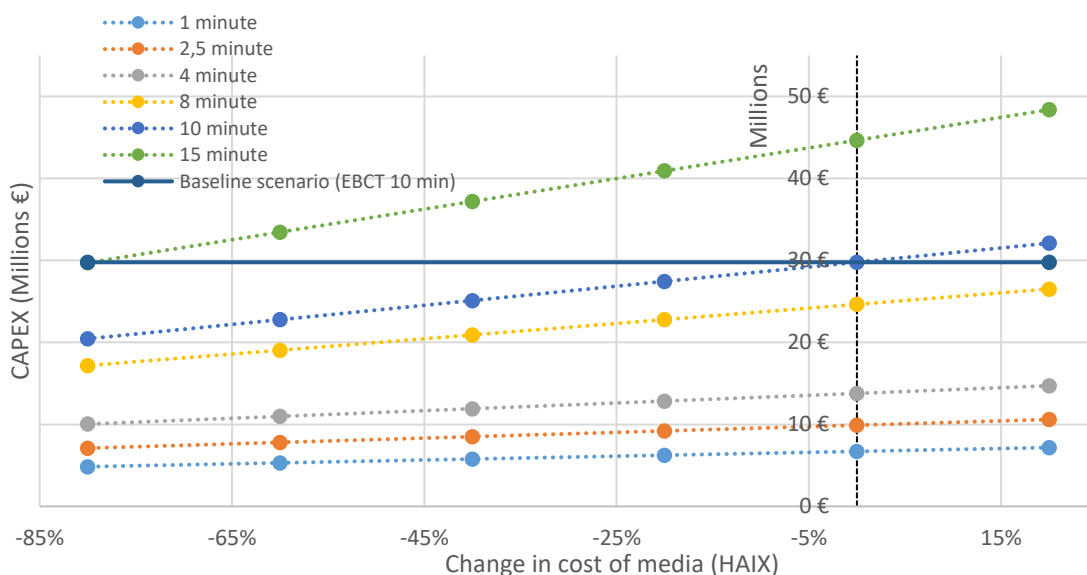


Figure 22. Change in CAPEX as a function of the change in the cost of phosphorus ion exchange resin (HAIX) and empty bed contact time (EBCT).

7.3.2.2. Change in the selling price of fertilisers

This section has assessed the impact of changes in the selling price of the two fertilisers obtained in the process, (i.e., hydroxyapatite and ammonium sulphate), on the total net cost of the project and on the revenues obtained. Variations in prices of $\pm 20\%$ have been considered.

The results obtained in figure 23 show that a change in the selling price of ammonium sulphate has a greater impact on total revenues compared to hydroxyapatite. This is because the price of ammonium sulphate is higher and also a higher amount is recovered compared to hydroxyapatite. For example, by increasing the selling price of ammonium sulphate by 8%, a 6.7% increase in total revenue is observed. On the other hand, an 8% increase in the selling price of hydroxyapatite only results in a 1.26% increase in total revenues compared to the baseline scenario. This suggests that changes in the price of hydroxyapatite have a lower impact on revenue generation compared to ammonium sulphate.

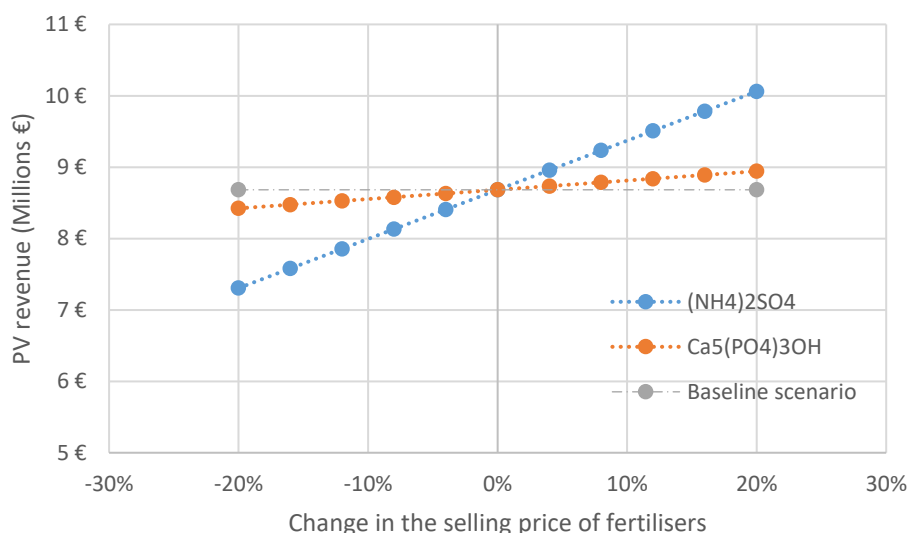


Figure 23. Change in the selling price of fertilisers as a function of PV revenue.

On the other hand, figure 24 shows the impact of a change in the price of each fertiliser on the total net cost. The results obtained, as expected, reveal that a change in the selling price of ammonium sulphate has a slightly higher impact on the total net cost compared to hydroxyapatite. For example, increasing the selling price of ammonium sulphate by 8% results in a 0.68% decrease in total net cost, while an 8% increase in the selling price of hydroxyapatite results in a 0.13% decrease in total net cost. However, it is important to note that both price changes have a relatively low impact on the total net cost of the project.

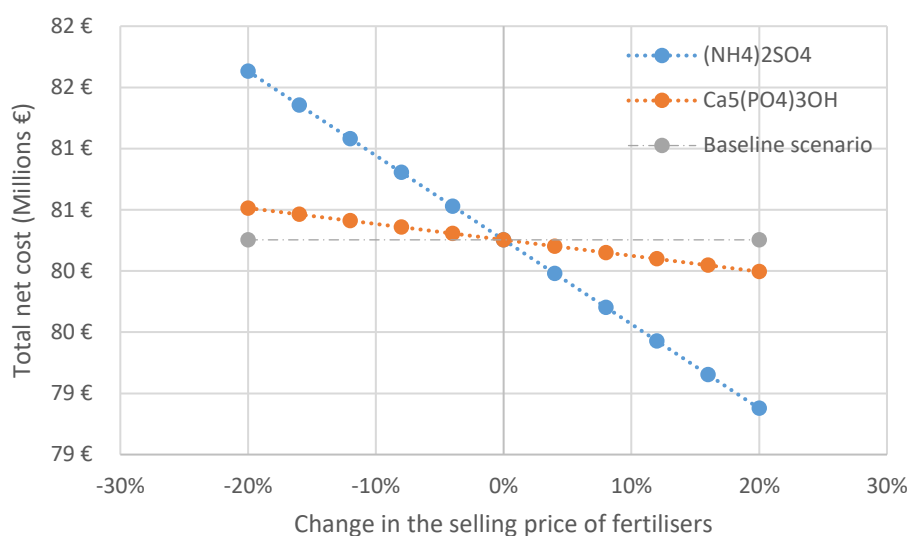


Figure 24. Change in the selling price of fertilisers as a function of the total net cost.

In conclusion, the results obtained suggest that the change in fertiliser prices is not a determining factor in the total net cost of the project.

7.3.2.3. Change in equipment and operational costs

Finally, the impact of changing the cost of major process equipment (e.g., ion exchange columns and resins) and key operating expenses (e.g., maintenance, labour, chemical costs, and electricity) on the total net cost of the project was evaluated. A $\pm 30\%$ variation in the cost of each item from the baseline case was considered. This allowed to determine which component has a greater influence on the economic results.

The results obtained are shown in figure 25.

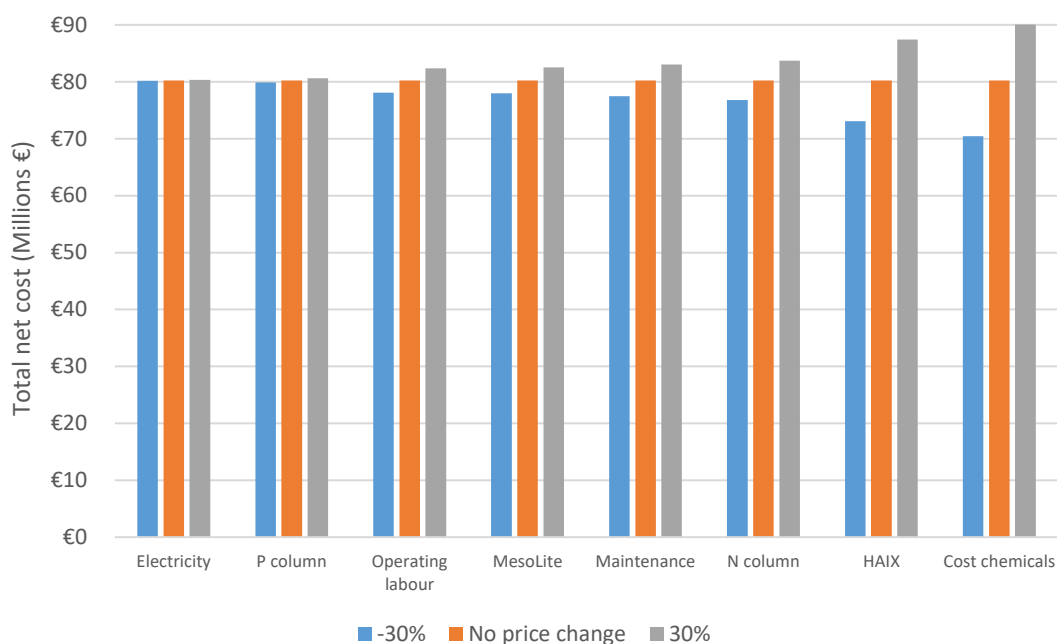


Figure 25. Impact of variation ($\pm 30\%$) in the cost of the most important economic parameters.

The impact of each item analysed on the net cost of the system is presented below:

1. Cost of electricity: The variation in the cost of electricity has the smallest impact on the total net cost, representing only a 0.1% variation. This indicates that fluctuations in electricity prices have a relatively low influence on the overall economic result.
2. Phosphorus ion exchange column: Changes in the cost of this columns have been identified as causing a 0.5% variation in the total net cost. While this impact is greater than that of electricity, it is still considered relatively low compared to other components.
3. Cost of operating labour: It is observed that variations in the cost of operating labour generate an impact of 2.7% on the total net cost. This indicates that changes in labour costs have a higher effect on the economic outcome of the project compared to electricity and the phosphorus ion exchange column.
4. Nitrogen ion exchange resin (MesoLite): Variations in the cost of the MesoLite have been determined to cause a 2.9% variation in the total net cost. These results indicate that this equipment has a significant impact on the economic result.
5. Maintenance costs: It is observed that maintenance costs have a greater influence on the net cost, generating a variation of 3.5%. This indicates that fluctuations in maintenance costs can have a considerable impact.
6. Nitrogen ion exchange column: Changes in the cost of this column have been found to cause a 4.3% variation in the total net cost. This indicates that this column has a significant influence on the economic result and requires special attention.

7. Phosphorus ion exchange resin (HAIX): It is noted that this item has a high impact, as a $\pm 30\%$ variation in the cost of the resin causes 9% variation in the total net cost. This highlights the importance of controlling the costs associated with the phosphorus ion exchange resin to ensure the lowest impact on the economic results of the project.
8. Chemical costs: Chemical costs have been identified as having the greatest impact on the total net cost of the project, with a variation of 12.2% when there is a change in cost of $\pm 30\%$. This emphasises the need to efficiently manage chemicals in the process.

In summary, these results provide a holistic view of how changes in the main system items can influence the net cost of the project. These findings enable strategic decisions to be made to efficiently manage resources, mitigate risks, and minimise total project cost.

8. Conclusions

The economic feasibility of implementing ion exchange technologies to recover nitrogen and phosphorus from municipal wastewater has been evaluated. The results obtained provided important conclusions for the advancement of the circular economy and sustainable water treatment.

Ion exchange technologies have been shown to have great potential for converting nutrients in wastewater into valuable fertilisers. The design and economic analysis of the proposed alternative, which combines ion exchange with membrane and precipitation technologies, has demonstrated the feasibility of this approach. The case study considered in this work is based on an operating capacity of 20,000 m³ day⁻¹ of municipal wastewater with a concentration of 56 mg L⁻¹ NH₄-N and 14 mg L⁻¹ PO₄-P. The proposed treatment system utilizes fixed bed resin columns, which allow the wastewater to pass through until saturation is reached. The resin is then regenerated, while another set of columns ensures continuous treatment. This approach efficiently removes and recovers ammonium and phosphorus from the wastewater stream.

However, it is important to note that other alternatives combining ion exchange with different complementary technologies, which could include the integration of adsorption processes, more selective membranes, or advanced filtration technologies, should be further investigated and explored to improve the overall treatment efficiency and maximise nutrient recovery.

The economic analysis results showed that a net cost of 80,254,366 € was obtained, with a low contribution of the incomes on the final results. These results could suggest that the process is not economically viable in strictly financial terms. However, it is important to consider other broader aspects and benefits that may influence the viability of the project.

Firstly, the main objective of the wastewater treatment plant is to remove nutrients. This implies that the value of the project lies in the environmental and sustainable aspect, rather than in the generation of direct income. The environmental benefits associated with improved water quality have an indirect value in terms of conservation of natural resources and prevention of environmental damage.

In addition, compliance with environmental regulations is a key factor for wastewater treatment plants. If the project enables compliance with the required standards and avoids possible sanctions or fines, this can also have a positive financial impact.

Another relevant aspect is the adoption of circular economy approaches. The recovery of nutrients for use as fertilisers contributes to resource management and reduces dependency on external sources of

fertilisers. Although these benefits may be difficult to quantify directly, they contribute to the long-term sustainability and resilience of the agricultural system.

In relation to CAPEX, it was identified that the item with the highest cost contribution compared to the others is the hybrid anion exchange resin (HAIX) for phosphorus recovery, accounting for 39%. Therefore, it is crucial to carefully evaluate the alternatives available on the market and consider their performance, durability, and long-term operating costs. In addition, strategies can be explored to optimise the use of this resin, such as optimising regeneration and increasing its capacity.

On the other hand, the practice of reusing regenerant solutions to minimise chemical costs has proven to be a valuable strategy for achieving economic savings on the project. By recycling and reusing the regenerant, the expenses related to the purchase of chemicals can be significantly reduced, which ultimately improves the economic viability and sustainability of the entire process. This approach not only contributes to cost reduction, but also aligns with the principles of the circular economy by minimising resource consumption and waste generation.

However, it is important to note that despite the implementation of the reuse of regenerant solutions, chemical requirements still accounted for 55% of the total operating expenses. This finding highlights the importance of efficiently managing chemicals in the process. Exploring strategies to optimise chemical use, such as finding more efficient alternatives, can help to further reduce operating costs and improve project viability.

The individual economic analysis of the nitrogen section concluded that this section represents 51% of the total net cost of the plant, and a recovery cost of $6.81 \text{ € kg}^{-1} \text{ NH}_4\text{-N}$ was obtained. Compared to other reference studies, disparities are observed in the nitrogen recovery costs obtained with ion exchange technologies and with conventional removal methods. These differences can be attributed to the scale of the project, the mode of operation, the efficiency and treatment objectives of each project, as well as additional economic factors.

Regarding the phosphorus section, it was concluded that it contributes 49% to the total net costs of the plant, and a recovery cost of $27.21 \text{ € kg}^{-1} \text{ PO}_4\text{-P}$ was obtained. Compared to conventional wastewater phosphorus recovery processes, disparities are observed that can be attributed to differences in the recovery mechanisms and chemical requirements involved, as well as the concentration of phosphorus in the different treated effluents.

In relation to the sensitivity analysis performed, it highlights the importance of the empty bed contact time (EBCT) and resin capacity on the costs and economic viability of the project. EBCT was found to play a crucial role in both initial equipment costs and operating costs over the lifetime of the plant. In

addition, resin capacity was found to have a greater impact on net process cost compared to resin lifetime, suggesting the need to increase resin capacity to provide longer cycles.

Finally, some future actions related to this study have been identified. It is recommended to carry out pilot- scale tests to evaluate the performance of the resins with different wastewater characteristics. It is also necessary to develop efficient large-scale cleaning and regeneration systems to understand the complexity of each step and to optimise the process.

In conclusion, this study confirms the feasibility of implementing ion exchange technologies for the recovery of nitrogen and phosphorus from municipal wastewater. Although some challenges and areas for improvement have been identified, this approach demonstrates its potential to move towards a circular economy and contribute to sustainable water treatment.

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Annex A

The main purpose of this annex is to present the mass balances, chemical requirements and the equations used to design the municipal wastewater treatment plant.

A1. Mass balances

Wastewater treatment

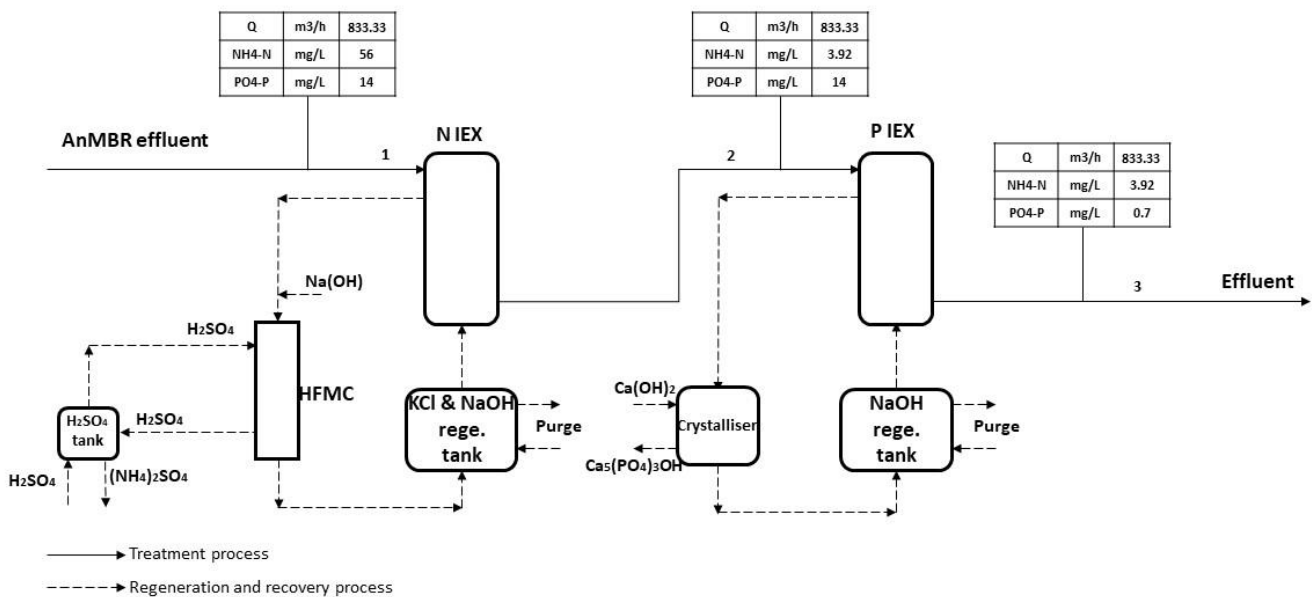


Figure 26. Mass balance of the wastewater treatment process.

From the input characteristics of the wastewater, the output concentrations of each nutrient have been calculated according to the following equation:

$$C_{out i} = C_{in i} * (1 - \eta_{efficiency}) \quad (\text{Eq. 14})$$

Where $C_{out i}$ is the outlet concentration of nutrient i (mg L^{-1}), $C_{in i}$ is the inlet concentration of nutrient i (mg L^{-1}) and $\eta_{efficiency}$ is the removal efficiency of each column.

On the other hand, the design parameters related to this stage of the process can be found in tables 5 and 7 (adsorption stage).

Nitrogen regeneration and recovery section

All design parameters and regenerant composition related to this process stage can be found in table 6 (regeneration stage of the N section) and table 9 (parameters of the LLMC technology).

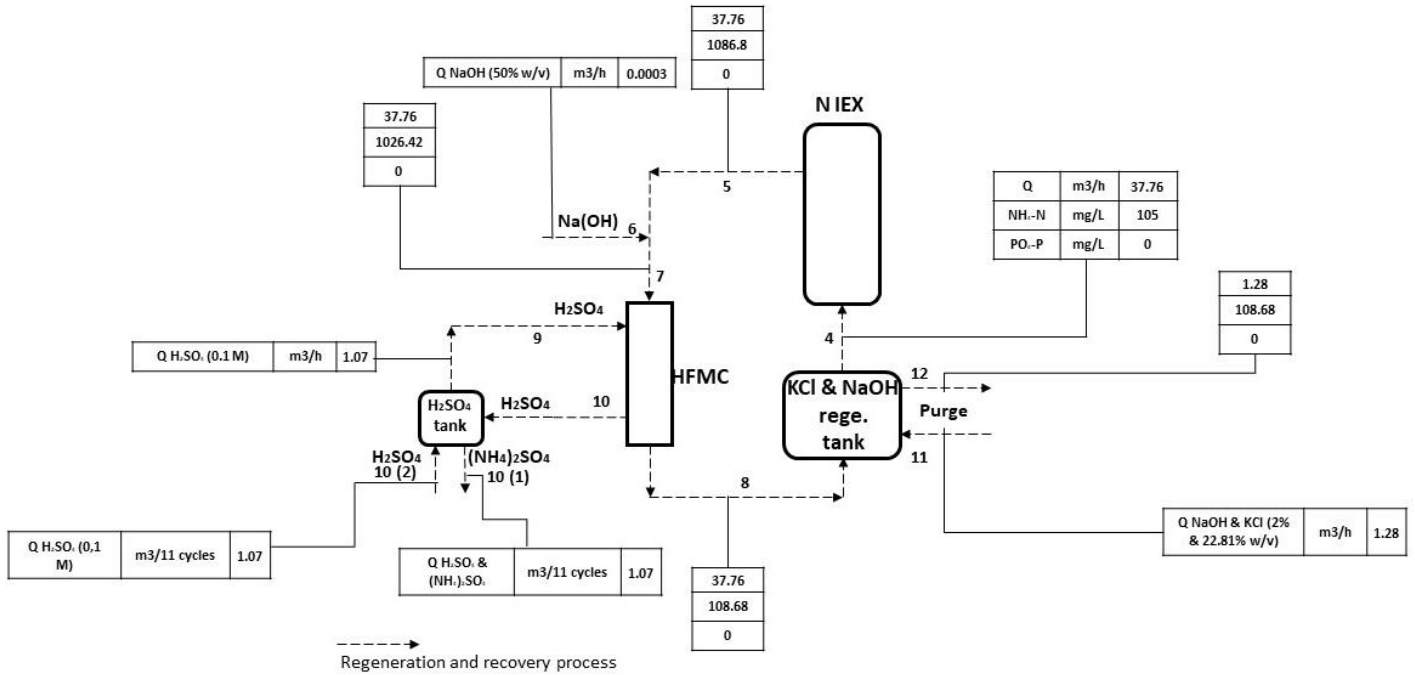


Figure 27. Mass balances of the nitrogen regeneration and recovery section.

The amount of regenerant required has been calculated according to the following equation:

$$Q_{regenerant} \left(\frac{m^3}{h} \right) = \frac{BV_{required} * Resin\ volume (m^3)}{Cycle\ time (h)} \quad \text{(Eq. 15)}$$

To calculate the amount of NaOH to be added in current 6, the following equations have been used, considering that the pH is to be raised from 7 (current 5) to 10 (current 7):

$$[OH^-]_5 = 10^{-7} \ \& \ [OH^-]_7 = 10^{-4} \quad \text{(Eq. 16)}$$

$$NaOH\ required \ (mol\ L^{-1}) = ([OH^-]_7 - [OH^-]_5) \quad \text{(Eq. 17)}$$

The amount of H₂SO₄ (9) required has been calculated in such a way that the following condition is fulfilled, to maintain an excess of H₂SO₄:

$$\frac{H_2SO_4\ in}{NH_3\ removed} \ (kg) \sim 30 \quad \text{(Eq. 18)}$$

Once this ratio reaches a value of 3 and thus $\text{pH} > 1.5$ (every 11 cycles), the acid solution is replaced by a new one.

To calculate the purge flow rate, the mass balance of the $\text{NH}_4\text{-N}$ component has been used. The maximum $\text{NH}_4\text{-N}$ concentration at the inlet of the ion exchange column (4) has been set to 105 mg L^{-1} .

$$Q_{12}(\text{m}^3 \text{ h}^{-1}) = \frac{Q_8 * C_{(8)\text{NH}_4\text{-N}} - Q_4 * C_{(4)\text{NH}_4\text{-N}}}{C_{(12)\text{NH}_4\text{-N}}} \quad (\text{Eq. 19})$$

Finally, to calculate the amount and concentrations of regenerant to be added (11) to maintain the necessary compositions for regeneration, the basic material balance equations have been used.

$$Q_8 * C_{(8)\text{regenerant}} + Q_{11} * C_{(11)\text{regenerant}} = Q_{12} * C_{(12)\text{regenerant}} + Q_4 * C_{(4)\text{regenerant}} \quad (\text{Eq. 20})$$

Phosphorus regeneration and recovery section

All design parameters and regenerant composition related to this process stage can be found in table 8 (regeneration stage of the P section) and table 10 (crystalliser technology).

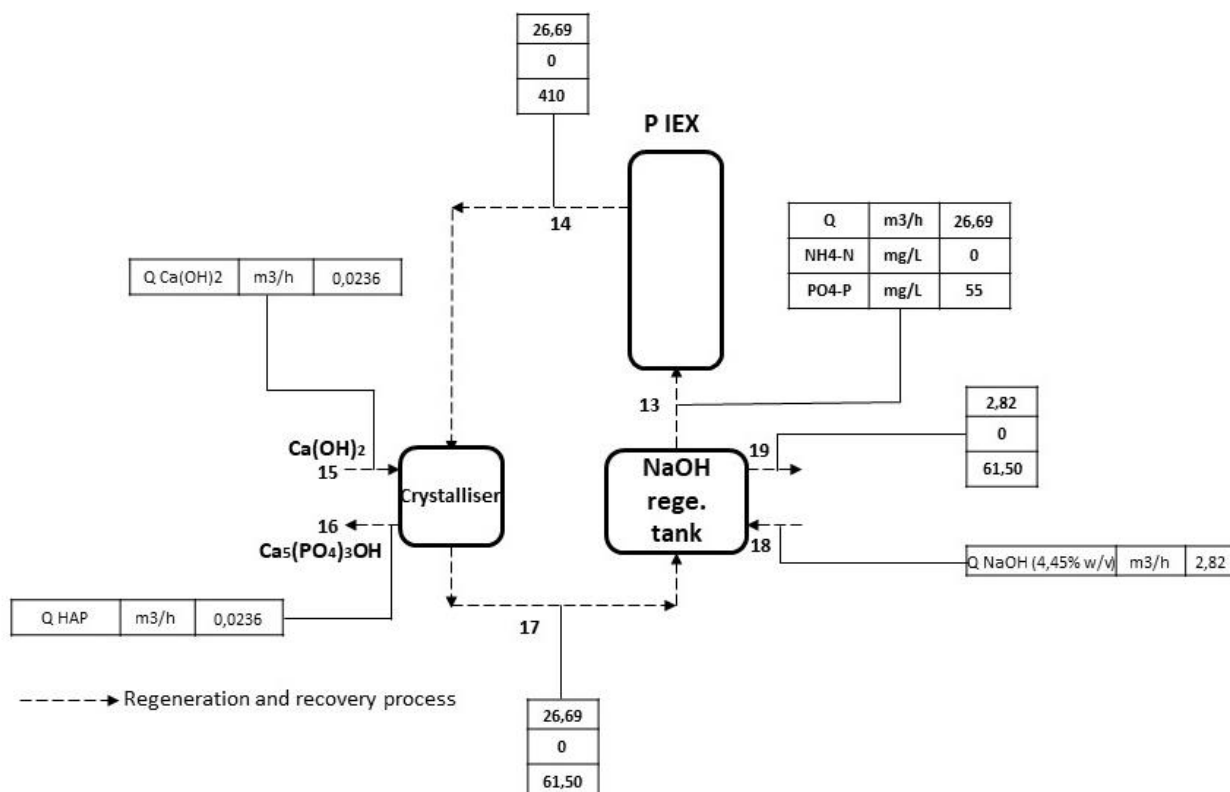


Figure 28. Mass balances of the phosphorus regeneration and recovery section.

The amount of regenerant required has been calculated according to the following equation:

$$Q_{regenerant} \left(\frac{m^3}{h} \right) = \frac{BV_{required} * Resin\ volume (m^3)}{Cycle\ time (h)} \quad (\text{Eq. 21})$$

The amount of hydrated lime (Ca(OH)₂) required has been calculated according to the following ratio:

$$Ca: P\ ratio (mol) = 2 \quad (\text{Eq. 22})$$

To calculate the purge flow rate, the mass balance of the PO₄-P component has been used. The maximum PO₄-P concentration at the inlet of the ion exchange column (13) has been set to 55 mg L⁻¹.

$$Q_{19} (m^3\ h^{-1}) = \frac{Q_{17} * C_{(17)PO_4-P} - Q_{13} * C_{(13)PO_4-P}}{C_{(19)PO_4-P}} \quad (\text{Eq. 23})$$

Finally, to calculate the amount of regenerant to be added (18), the basic material balance equations have been used.

$$Q_{17} * C_{(17)NaOH} + Q_{18} * C_{(18)NaOH} = Q_{19} * C_{(19)NaOH} + Q_{13} * C_{(13)NaOH} \quad (\text{Eq. 24})$$

A2. Design equations for fixed-bed ion exchange contactors

The design of ion exchange columns requires the determination of the volume of resin, the surface area of resin required, the number of columns, the breakthrough time and the pressure drop.

Volume of resin

The resin volume can be calculated from the service flow rate:

$$Total\ required\ resin\ volume (m^3) = \frac{Q (m^3\ s^{-1})}{SFR (BV\ s^{-1})} \quad (\text{Eq. 25})$$

Where Q is the treated water flow rate and SFR is the service flow rate.

Surface area of resin required

The total ion exchange surface area required is determined to be:

$$Total\ required\ surface\ area (m^2) = \frac{Resin\ volume (m^3)}{Resin\ depth (m)} \quad (\text{Eq. 26})$$

Number of columns

If the total column area is divided by the area of one column, the number of columns required can be calculated as:

$$\text{Required number of columns} = \frac{\text{Total column area (m}^2\text{)}}{\text{Area of one column (m}^2\text{)}} \quad (\text{Eq. 27})$$

Breakthrough time

The time it takes for the resin to saturate is calculated as follows:

$$\text{Breakthrough time (h)} = \frac{\text{Media capacity (g}_i \text{ kg}_{\text{resin}}^{-1}) * \text{Packing density resin (kg m}^{-3}\text{)} * \text{Resin volume (m}^3\text{)}}{\text{Treated water flow rate (L h}^{-1}\text{)} * \text{Difference in concentrations of } i \text{ (g}_i \text{ L}^{-1}\text{)}} \quad (\text{Eq. 28})$$

Where i is the species to be removed in each case.

Pressure drop Mesolite

The pressure drop of the Mesolite has been calculated from the pressure drop graph as a function of the treated flow and assuming that the behaviour of the zeolite-61 is identical to that of the Mesolite.

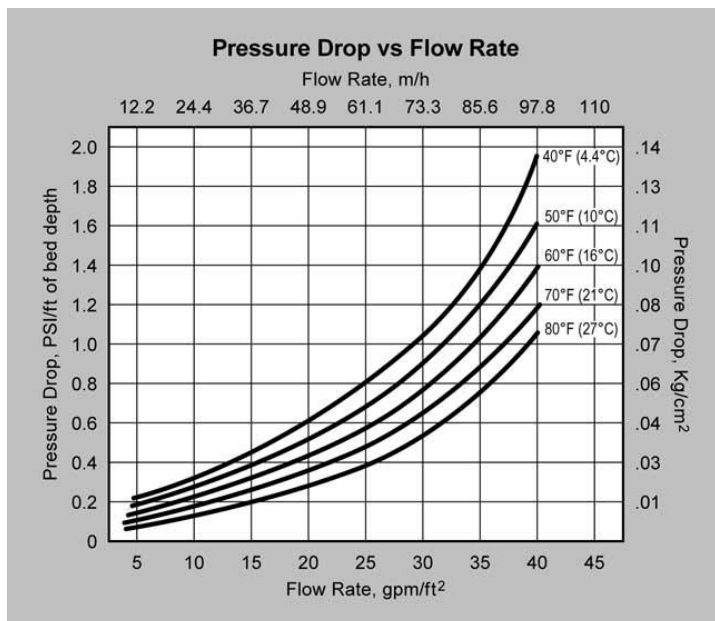


Figure 29. Pressure drop graph of Mesolite. (Zeolite-61)

Pressure drop HAIX

The pressure drop of the HAIX has been calculated from the pressure loss versus flow rate graph provided by the manufacturer of the hybrid anion exchange resin ASM-125. This resin and the resin used for phosphorus removal are considered to have similar behaviour.

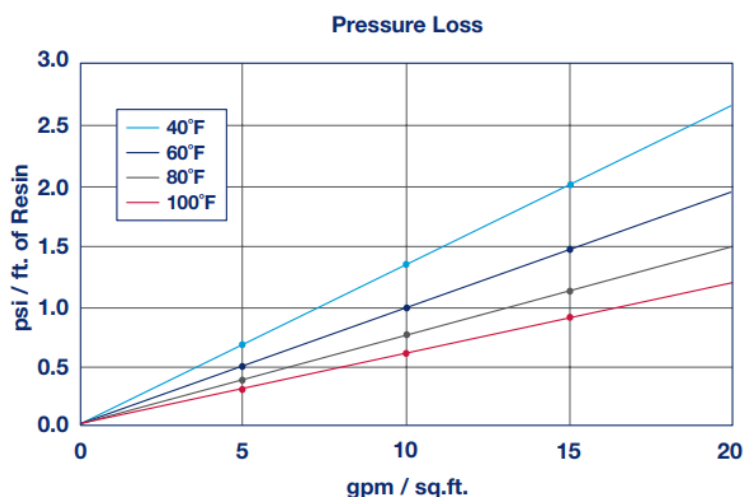


Figure 30. Pressure drop graph of HAIX. (ASM-125)

A3. Design equations for LLMC

Logarithmic mean concentration difference

$$\Delta C_{LM} \text{ (mol m}^{-3}\text{)} = \frac{(C_{liq\ in} - C_{gas\ out}) - (C_{liq\ out} - C_{gas\ in})}{\ln \left[\frac{(C_{liq\ in} - C_{gas\ out})}{(C_{liq\ out} - C_{gas\ in})} \right]} \quad \text{(Eq. 29)}$$

Mass transfer coefficient of the membrane

$$K_m \text{ (m s}^{-1}\text{)} = \frac{D_N * \epsilon * H}{L * T} \quad \text{(Eq. 30)}$$

Where D_N is the diffusivity of NH_3 ($m^2\ s^{-1}$), ϵ is the porosity of the membrane, H is the henry's constant, L is the approximate wall thickness of the membrane (m) and T is the pore tortuosity.

Table 23. Hollow fibre design parameters constant values. (Canellas-Garriga, 2018)

Parameter	Unit	Value
D_N (diffusivity of NH ₃)	$m^2 s^{-1}$	4.00E-06
ϵ (porosity of the membrane)		0.4
H (henry's constant)		6.50E-04
L (approx. wall thickness of the membrane)	m	6.50E-05
T (pore tortuosity)		2.5

Permeation flux of ammonia through the membrane

$$J_{A,Mem} (mol m^{-2} s^{-1}) = K_m * \Delta C_{LM} \quad (\text{Eq. 31})$$

Total area required

$$A_T (m^2) = \frac{N}{J_{A,Mem}} \quad (\text{Eq. 32})$$

Where N is the molar flow of ammonia across the membrane ($mol s^{-1}$).

Number of modules

$$\text{Number of modules} = \frac{A_T}{A_{Mem}} \quad (\text{Eq. 33})$$

Where A_{Mem} is the available area of the membrane (m^2).

Annex B

This annex provides the detailed calculations of the cash flows used in the estimation of the present value (PV) in the economic evaluation of the project.

Table 24. Cash flows obtained for the estimation of the present value (PV) over the 20-year life of the plant.

Year	1	2	3	4	5
OPEX	3,969,855 €	3,969,855 €	4,561,512 €	3,969,855 €	6,992,102 €
OPEX UPDATED	3,780,814 €	3,600,776 €	3,940,405 €	3,266,009 €	5,478,495 €
REVENUE UPDATED	625,364 €	595,585 €	567,224 €	540,213 €	514,488 €
OPEX - REVENUE UPDATED	3,155,450 €	3,005,190 €	3,373,181 €	2,725,796 €	4,964,006 €

Year	6	7	8	9	10
OPEX	3,969,855 €	4,561,512 €	3,969,855 €	6,992,102 €	3,969,855 €
OPEX UPDATED	2,962,367 €	3,241,781 €	2,686,954 €	4,507,171 €	2,437,146 €
REVENUE UPDATED	489,989 €	466,656 €	444,434 €	423,271 €	403,115 €
OPEX - REVENUE UPDATED	2,472,377 €	2,775,125 €	2,242,519 €	4,083,900 €	2,034,031 €

Year	11	12	13	14	15
OPEX	4,822,970 €	3,969,855 €	6,992,102 €	3,969,855 €	4,561,512 €
OPEX UPDATED	2,819,891 €	2,210,564 €	3,708,061 €	2,005,046 €	2,194,165 €
REVENUE UPDATED	383,919 €	365,637 €	348,226 €	331,644 €	315,851 €
OPEX - REVENUE UPDATED	2,435,971 €	1,844,926 €	3,359,834 €	1,673,402 €	1,878,313 €

Year	16	17	18	19	20
OPEX	3,969,855 €	6,992,102 €	3,969,855 €	4,561,512 €	3,969,855 €
OPEX UPDATED	1,818,636 €	3,050,631 €	1,649,556 €	1,805,145 €	1,496,196 €
REVENUE UPDATED	300,811 €	286,486 €	272,844 €	259,851 €	247,477 €
OPEX - REVENUE UPDATED	1,517,825 €	2,764,144 €	1,376,712 €	1,545,293 €	1,248,718 €

