



Agricultural products from algal biomass grown in piggery wastewater: A techno-economic analysis

Elena M. Rojo ^{a,b}, María Molinos-Senante ^{a,b}, A. Alejandro Filipigh ^{a,b}, Tomás Lafarga ^c, F. Gabriel Acién Fernández ^c, Silvia Bolado ^{a,b,*}

^a Institute of Sustainable Processes, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain

^b Department of Chemical Engineering and Environmental Technology, School of Industrial Engineering, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain

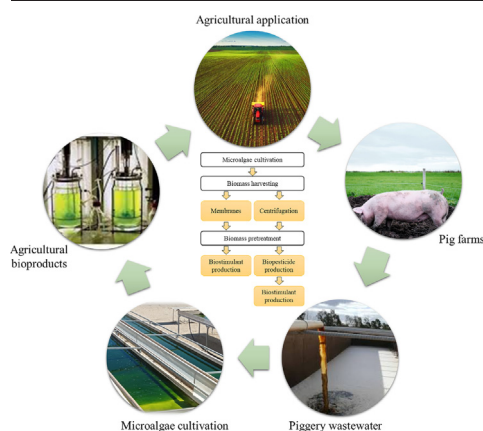
^c Department of Chemical Engineering, University of Almería, Carr. Sacramento, s/n, 04120 Almería, Spain



HIGHLIGHTS

- Valorization of piggery wastewater as agricultural products using photobioreactors
- Comparison of using membranes and centrifugation in product concentration and costs
- Competitive prices by ha of fertilization with biostimulants from algal biomass
- High equipment and operation costs of biopesticide production by solvent extraction
- Dependence on economic viability of type of harvesting, plant capacity and distance

GRAPHICAL ABSTRACT



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ABSTRACT

The intensification of livestock activities lead to an increase in waste generation with high content of nutrients, as is the case of piggery wastewater. However, this type of residue can be used as culture media for algae cultivation in thin-layer cascade photobioreactors to reduce its environment impact and produce a valorizable algal biomass. Biostimulants were produced by enzymatic hydrolysis and ultrasonication of microalgal biomass, using membranes (Scenario 1) or centrifugation (Scenario 2) as harvesting methods. The co-production of biopesticides by solvent extraction was also evaluated using membranes (Scenario 3) or centrifugation (Scenario 4). The four scenarios were analyzed by a technoeconomic assessment estimating the total annualized equivalent cost and the production cost, i.e., the minimum selling price. Centrifugation provided biostimulants approximately 4 times more concentrated than membranes, but with higher expense due to the cost of the centrifuge (contribution of 62.2 % in scenario 2) and the electricity requirements. The biopesticide production resulted the highest contribution to investment cost in scenarios 3 and 4 (34 % and 43 % respectively). The use of membranes was also more advantageous to produce biopesticides, although it was 5 times more diluted than using centrifuge. The biostimulant production cost was 65.5 €/m³ with membranes and 342.6 €/m³ by centrifugation and the biopesticide production cost was 353.7 €/m³ in scenario 3 and 2,122.1 €/m³ in scenario 4. Comparing the treatment of 1 ha of land, the cost of the biostimulant produced in the four scenarios was lower than the commercial one (48.1 %, 22.1 %, 45.1 % and 24.2 % respectively). Finally, using membranes for biomass harvesting allowed economically viable plants with lower capacity and longer distance

* Corresponding author at: Department of Chemical Engineering and Environmental Technology, University of Valladolid, Calle Dr. Mergelina s/n, 47011 Valladolid, Spain.
E-mail address: silvia.bolado@uva.es (S. Bolado).

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for biostimulant distribution (up to 300 km) than centrifuge (188 km). The algal biomass valorization for agricultural products production is an environmentally and economically feasible process with the adequate capacity of the plant and distribution distance.

1. Introduction

The exponential growth of the world's population is increasing the demand for animal products, leading also to an increase in animal manure generation, highlighting pig manure which has become a huge problem for the environment (Li et al., 2020). The European Union (EU) has around 148 million of pig heads which generate between 215 and 430 m³/year of piggery wastewater (PWW) (Ferreira et al., 2021) that must be treated to reduce its environmental impact. This type of residue is rich in organic matter (2,000–30,000 mg/L biological organic demand), nitrogen (200–2,055 mg/L), phosphorus (100–620 mg/L), and ammonium (110–1,650 mg/L) (Nagarajan et al., 2019) which can be used as nutrients for microalgae and bacteria consortium growth in a promising process with wastewater treatment photobioreactors (Rossi et al., 2022).

This treatment technology is considered a sustainable and green process and has several advantages over other conventional methods (direct application in land, waste stabilization ponds, anaerobic digestion, aerobic/anaerobic/anoxic systems, etc.) including reduction of greenhouse gases and the possibility to establish a biorefinery process within the circular economy (Nagarajan et al., 2019). Also, this technology allows to reduce the costs associated with nutrients requirements for microalgae production and the energy demand (Navarro-López et al., 2020a). After the PWW treatment, a biomass formed by microalgae and bacteria with a high content of proteins, carbohydrates and lipids is obtained and can be employed as a feedstock to produce commercial products for agriculture like biostimulants or biopesticides (Ferreira et al., 2021; Navarro-López et al., 2020b) as an alternative to chemical fertilizers and pesticides.

Biostimulants are compounds that promote the growth and quality of crops, improve mineral nutrient uptake and the tolerance to abiotic stress (du Jardin, 2015; Navarro-López et al., 2020a). On the other hand, biopesticides are substances produced naturally which are employed to control pests in agricultural crops and protect plants against pathogens (Asimakis et al., 2022; Fernández et al., 2021). Within biostimulants, those obtained from algae biomass have gained much attention in recent years due their high content of active compounds such as peptides/amino acids and plant hormones (cytokinins, auxins, gibberellins...) responsible for biostimulating activity of plants (Navarro-López et al., 2020a; Ranglová et al., 2021). Moreover, microalgae have antimicrobial and herbicidal compounds that are effective against pathogenic bacteria and biotic stress (Fernández et al., 2021; Ferreira et al., 2021). Ferreira et al. (2021) produced biostimulants and biopesticides from three different biomasses (*Tetradismus obliquus*, *Chlorella protothecoides*, *Chlorella vulgaris*) grown in PWW and found an overall increase on germination index (up to 138 % in cucumber seeds) of microalgae-treated crops. Also, all the microalgae provided biopesticides which inhibited the fungus growth of *Fusarium oxysporum* up to 40 %. Navarro-López et al. (2020b) studied the influence of the biostimulants obtained from *Scenedesmus* sp. after a high-pressure homogenization (HPH) on the germination index of watercress seeds, improving it by almost 10 % and Amaya-Santos et al. (2022) proved the germination index enhancement of watercress seeds and the high development of roots in soybeans with microalgae extracts of *Chlorella vulgaris* obtained after sonication at 280 W. Finally, Ranglová et al. (2021) demonstrated the biopesticide effect of extract of microalgae biomass grown in wastewater. They found a significant increase of the antibacterial and antifungal activities of *Chlorella vulgaris* grown in municipal wastewater, compared to the same strain grown in synthetic media.

The treatment of the PWW and biomass production can be carried out in open photobioreactors (Arora et al., 2021; Llamas et al., 2021), followed by a harvesting process for the recovery of the obtained biomass. Thin-layer is

an open photobioreactor which allows to achieve good results in the PWW treatment, since it maximises light availability in this coloured media thanks to the low culture depth (Ciardi et al., 2022). Centrifugation is usually employed in biomass harvesting due to its high efficiency (>90 %) and final solid concentration (12–22 %) (Arora et al., 2021), although the investment and the energy consumption is also high (about 1 kWh/m³) which can be reduced to 0.2 kWh/m³ by using membranes (Zhao et al., 2023). This technology has several advantages including continuous separation, easily up-scale, 100 % biomass retention and mild operation conditions which makes it a promising technology for biomass harvesting.

Few articles have investigated the economic viability of the valorization of algal biomass to produce biostimulants or biopesticides. To the best of our knowledge, only Romero-García et al. (2022) evaluated the economics of the production of a biofertilizer concentrated in amino acids (6 %) from microalgal biomass generated in an urban wastewater treatment plant, being economically feasible. The scarce techno-economic studies about valorization of algal biomass focus on the cultivation process in photobioreactors and the production of biofuels (Bhatt et al., 2022; Wilson et al., 2021). The results show a high variation in costs related to the type of photobioreactor used, the species of microalgae, the downstream process, operating conditions, etc. As examples, the cost estimates for cultivation process were 3.2–11.0 €/kg of microalgal biomass and for biodiesel production was 0.6–9.0 €/L (Slegers et al., 2020). It highlights the necessity of estimating the costs for each specific process (Vázquez-Romero et al., 2022) to obtain certain bioproducts such as biostimulants or biopesticides to be feasible from a technical, economic, and environmental perspective (Fernández-Delgado et al., 2022).

This paper is aimed at the techno-economic analysis of producing biostimulants and biopesticides from a microalgal biomass grown in a thin-layer photobioreactor treating PWW comparing two types of harvesting and separation methods (membrane and centrifuge) and its influence on the economics of the process. This information allows estimating the production costs of the biostimulant produced which will be compared to commercial products. A sensitivity analysis was also performed to study the parameters that most affect the designed process.

2. Material and methods

This section describes the operational parameters and the calculation basis used to carry out the research of this paper for the cultivation of microalgae biomass and its valorization to obtain biostimulants (by enzymatic hydrolysis) and biopesticides (by solvent extraction) based on previous data and published articles. Likewise, a techno-economic assessment was performed to estimate the total annualized equivalent cost and the production cost, which allows to determine the minimum selling price of the agricultural products.

2.1. Process design

2.1.1. Raw material

PWW was used as raw material in the process. The composition of a sample of PWW from the municipality of Cuéllar (Spain) was indicated in the following Table 1 (Collao et al., 2022):

The total PWW flow treated was 37.77 m³/d considering two pig farms with ≈ 3,200 heads and that one head pig produced annually approximately 2.15 m³ of slurry, both average values in the municipality of Cuéllar (Spain) (PRTR España, 2022). This wastewater was diluted by 10 % with fresh water and recirculation water (Section 2.1.2.) to avoid ammonium inhibition in the biomass growth (Villaró et al., 2022).

Table 1
Composition of the PWW used in the study.

Parameter	Concentration (mg/L)
Total suspended solids (TSS)	8,400
Total organic carbon (TOC)	14,260
Total nitrogen (TN)	5,120
Ammonia nitrogen (AM)	3,328
Total phosphorus (TP)	76

2.1.2. Thin layer photobioreactor

PWW treatment was carried out in an open thin-layer cascade photobioreactor operating at the optimized operational conditions

selected from previously published works (Ciardi et al., 2022; Villaró et al., 2022): 50 % of culture water recirculation, dilution rate 0.33 days^{-1} , final dry biomass concentration of 2 g/L , water losses due to evaporation of $5 \text{ L/m}^2/\text{d}$ and a culture depth of 4 cm . The photobioreactor operated during 24 h per day and the pH was maintained at 8 by on-demand injection of CO_2 (Ciardi et al., 2022). Nutrients removal after the microalgae treatment was established at 90 %, 60 % and 60 % for TOC, TN, and TP respectively (Collao et al., 2022) and the microalgae biomass produced in the photobioreactor was composed by 51.7 % of proteins, 22.3 % of carbohydrates and 13.4 % of lipids in dry basis (values obtained on a pilot scale in a thin-layer photobioreactor fed with 10 % slurry) (Villaró et al., 2022).

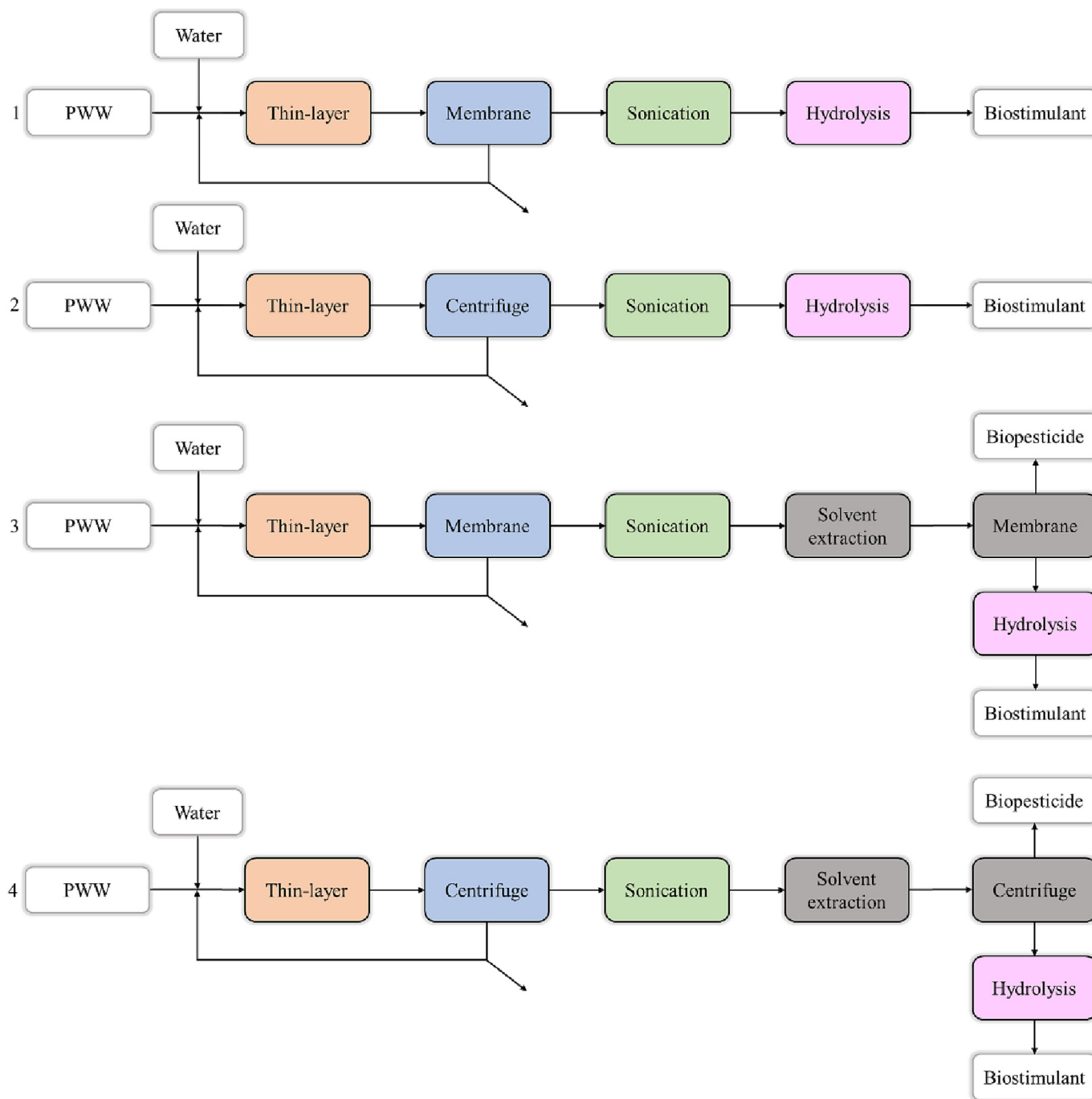


Fig. 1. Block diagrams of each studied scenario. 1) Scenario 1; 2) Scenario 2; 3) Scenario 3; 4) Scenario 4. Microalgae cultivation (orange box), biomass harvesting (blue box), biomass pretreatment (green box), biostimulant production (pink box) and biopesticide production (grey box).

2.1.3. Scenarios

Four different scenarios were evaluated in this study (Fig. 1). Scenario 1 consisted of the production of biostimulants after biomass harvesting with a membrane system followed by a sonication pretreatment and an enzymatic hydrolysis while scenario 2 used a centrifuge for biomass harvesting and the rest of the process was similar to Scenario 1. Scenarios 3 and 4 consisted of the production of biopesticide by a solvent extraction and biostimulant production by an enzymatic hydrolysis after biomass harvesting and posterior solvent extraction separation with membrane systems (scenario 3) or centrifuge (scenario 4). At the end of all the processes, phosphate was added to the biostimulant to preserve the product and to achieve a N/P ratio (12/24) similar to commercial fertilizers.

More detailed process flow diagrams, with all the auxiliary equipment, are included in the Supplementary Material (Figs. S.1, S.2, S.3, S.4). The operation conditions in each scenario are summarized in the Table 2 based on previous research (Arora et al., 2021; Morillas-España et al., 2022; Morillas-España et al., 2021; Navarro-López et al., 2020a, 2020b; Romero-García et al., 2022) and global and elemental mass balances are presented in the Supplementary Material (Tables S.1, S.2, S.3, S.4).

2.2. Techno-economic analysis

An economic assessment was performed for the four scenarios using as a design basis, a plant with a treatment capacity of 37.77 m³/d of PWW (Section 2.1.1.) considering a price of 0 €/m³ as residue. To evaluate the total cost of the processes, the total annualized equivalent cost (TAEC) was determined with Eq. (1) (González-Viar et al., 2016). This economic indicator is widely used in techno-economic analysis of different wastewater treatment processes (Sun et al., 2020). The production costs for both bioproducts (biostimulant and biopesticide) which allows to recover the total costs and therefore, it can be considering as the minimum selling price, was determined based on the TAEC and final bioproduct production (Eq. (2)). Moreover, the comparison of the estimated production cost with

typical prices for a commercial fertilizer informs about the economic feasibility of the evaluated technology:

$$TAEC \left(\frac{\text{€}}{\text{year}} \right) = \frac{r \cdot (1+r)^t}{(1+r)^t - 1} \cdot IC + OMC \quad (1)$$

$$\text{Production cost} \left(\frac{\text{€}}{\text{m}^3} \right) = \frac{TAEC}{P} \quad (2)$$

where TAEC was the total annualized equivalent cost (€/year), IC was the investment cost with fixed capital (€), OMC were the operational and maintenance costs (€/year), r was the discount rate (5 %), t was useful life of the project (10 years), and P was the bioproduct production (m³/year). In scenarios 3 and 4, biostimulant production cost was set at the same value as obtained in scenarios 1 and 2 respectively, to subsequently determine the production cost of the biopesticides.

2.2.1. Investment cost (IC)

IC included the total equipment cost (TEC), the fixed capital and the fix capital per year. The TEC for biomass harvesting, biomass pretreatment, biostimulant and biopesticide production was determined based on equipment costs reported in ASPEN HYSYS V12 considering the inflation rate until 2022 in United States of America (10.5 %), while TEC for biomass cultivation was determined according to Ación et al. (2012) also considering the inflation rate until 2022 in Spain (12.9 %) and scaled according to the size, compared to the reference size of a quoted item according to Eq. (3) (Rossi et al., 2022):

$$Cost_2 = Cost_1 \cdot \left(\frac{Size_2}{Size_1} \right)^R \quad (3)$$

where Cost₁ was the cost for a reference item/equipment (€), Cost₂ was the cost of the equipment with a different size (€), Size₁ was the size of the reference equipment, Size₂ was the size of the target equipment, and R was the

Table 2

Summary of the operational parameters and conditions associated to each scenario considered in the techno-economic analysis.

Scenario	1	2	3	4
Biomass harvesting	<i>Membrane</i> Efficiency = 100 % Solid losses = 5 % Retentate solid concentration = 20 g/L Flux = 40 L/m ² /h	<i>Centrifuge</i> Efficiency = 95 % Retentate solid concentration = 90 g/L	<i>Membrane</i> Efficiency = 100 % Solid losses = 5 % Retentate solid concentration = 20 g/L Flux = 40 L/m ² /h	<i>Centrifuge</i> Efficiency = 95 % Retentate solid concentration = 90 g/L
Biomass pretreatment	<i>Sonication</i> P = 400 W t = 10 min	<i>Sonication</i> P = 400 W t = 10 min	<i>Sonication</i> P = 400 W t = 10 min	<i>Sonication</i> P = 400 W t = 10 min
Biostimulant production	<i>Enzymatic hydrolysis</i> Protease enzymes [Enzyme] = 2 % w/W _{dry biomass} t = 240 min T = 50 °C pH = 7 Agitation = 1 kWh/m ³	<i>Enzymatic hydrolysis</i> Protease enzymes [Enzyme] = 2 % w/W _{dry biomass} t = 240 min T = 50 °C pH = 7 Agitation = 1 kWh/m ³	<i>Enzymatic hydrolysis</i> Protease enzymes [Enzyme] = 2 % w/W _{dry biomass} t = 240 min T = 50 °C pH = 7 Agitation = 1 kWh/m ³	<i>Enzymatic hydrolysis</i> Protease enzymes [Enzyme] = 2 % w/W _{dry biomass} t = 240 min T = 50 °C pH = 7 Agitation = 1 kWh/m ³
Biopesticide production		-	<i>Solvent extraction</i> [Solvent] = 40 % v/v t = 60 min T = room Yield = 10 % <i>Membrane</i> Efficiency = 100 % Solid losses = 5 % Retentate solid concentration = 20 g/L Flux = 40 L/m ² /h <i>Flash evaporation</i> Solvent recovery = 94 % T = 96.5 °C P = 1 atm φ = 0.83	<i>Solvent extraction</i> [Solvent] = 40 % v/v t = 60 min T = room Yield = 10 % <i>Centrifuge</i> Efficiency = 95 % Retentate solid concentration = 90 g/L <i>Flash evaporation</i> Solvent recovery = 94 % T = 96.5 °C P = 1 atm φ = 0.83

cost exponent (0.85) (Ación et al., 2012). The fixed capital and the fix capital per year were then calculated according to Lang's Factor method considering a solid-liquid process (Pérez et al., 2021). This method is widely used in the industrial engineering to estimate the final IC in an industrial plant.

2.2.2. Operational and maintenance costs (OMC)

OMC included the raw material necessities (which was determined based on the mass balances), energy requirements (for pumps, centrifuges, mixers, ultrasounds, membrane filtration) and labor. Energy requirements were established as 1 kWh/m³ for the centrifuge, 19 W/m³ for thin-layer mixer, 1 kWh/m³ for reactor mixers, 13.89 kWh/kg_{biomass} for sonication and 0.2 kWh/m³ for membrane filtration (Ación et al., 2012; Pérez et al., 2021; Zhao et al., 2023) considering an electricity price of 0.25 €/kWh (average price in Spain the last trimester of 2022) (ESOIS, 2022). The raw material required for the process included, water (0.05 €/m³), CO₂ (0.1 €/kg), enzymes (10 €/kg), solvent (0.6 €/m³), low pressure steam (0.14 €/kg) and phosphate (0.5 €/kg). All these prices were obtained from literature (ChemAnalyst, 2022; Llamas et al., 2021; Pérez et al., 2021; Quiroz-Arita et al., 2022; Romero-García et al., 2022).

2.3. Comparison with commercial products

The annual cost of treating 1 ha of land (€/ha-year) was estimated based on biostimulants produced from PWW and a commercial fertilizer (Fercampo S.A., 2022). It allows evaluating the economic feasibility of producing biostimulants from PWW. For this purpose, the amount of nutrients (C, N and P) and biostimulant (L/ha) necessary to obtain the same values and ratios of the commercial fertilizer was determined, according to the composition of the bioproduct obtained. The cost of transporting the biostimulants (€/ha-year) was also included in the assessment, considering the use of diesel trucks of 2.5 T for scenarios 2 and 4, and 10 T for scenarios 1 and 3 (diesel price set at 1.78 €/L (Global Petrol Prices, 2023)) with fuel consumptions of 0.08 and 0.18 L/km, respectively (Jin et al., 2022). The operating cost was assumed to be 10 €/hour including transportation time and 1 h for loading and unloading (Metson et al., 2020). Finally, the minimum plant capacity necessary to achieve a feasible process was also determined by recalculating equipment and operating costs based on capacity. Experiments are running to compare dosage and effect of biopesticide extracts from microalgae biomass with commercial pesticides, but data are not available at this time. Therefore, comparison of this new bioproduct with the commercial alternatives was not possible currently.

2.4. Sensitivity analysis

A sensitivity analysis for the main operational parameter of the process and the most relevant consumables and commodities (PWW flow rate, electricity cost, and steam cost for heating) was performed to study their influence on the final economic analysis and test the robustness of the process against different changes. PWW flow rate was varied by ± 10 % for the sensitivity analysis, while electricity and steam cost were varied according to the prices observed in the last trimester of 2022 (Table S.5).

3. Results

The results obtained from the techno-economic assessment of each of the studied scenarios are described and discussed in the following subsections.

3.1. Biostimulant production

Different biostimulants were produced in each scenario, varying in concentration and in the total annual production based on the mass balances (Tables S.1, S.2, S.3, S.4) and the different removal efficiencies of TOC, TN and TP in the photobioreactor. As shown in Table 3, the biostimulant obtained in the scenario 2 (where a centrifuge was used for the biomass harvesting) had the highest concentration of carbon (4.59 % C), nitrogen

Table 3
Bioproduct composition and annual production in each scenario.

Biostimulant	Scenario 1	Scenario 2	Scenario 3	Scenario 4
C (%)	1.07	4.59	22.25	25.46
N (%)	0.24	0.83	0.22	0.85
P (%)	0.47	1.65	0.45	1.70
TSS (%)	1.99	8.85	1.99	8.85
Production (m ³ /year)	8,224	1,849	7,029	1,582
Biopesticide	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Production (m ³ /year)	–	–	790	165

(0.83 % N) and phosphorus (1.65 % P). These last two nutrients are the main components in the conventional fertilizers and stimulants and necessary for the proper growth of plants (Remya et al., 2021). The high biomass concentration efficiency of a centrifuge compared to the membrane system of scenario 1, results in a more concentrated product after the pretreatment with ultrasounds and the enzymatic hydrolysis to extract the biostimulant from the microalgae biomass produced in the thin-layer. This highest concentration entails the lowest volume production, with a value of 1,849 m³/year.

The highest volume production of 8,224 m³/year was achieved in the scenario 1 using the membrane system for the biomass harvesting which allows to obtain high water recovery rate and high-quality biomass upon concentration (Malaguti et al., 2022) but with the lowest nutrient concentrations (1.07 % of C, 0.24 % of N and 0.47 % of P). The difference in nutrient ratios between scenario 1 and 2 was due to the content of dissolved N in the treated water. In the photobioreactor, the C removal efficiency (90 %) was higher than the N removal (60 %). The simultaneous production of biostimulants and biopesticides after the biomass harvesting and posterior solvent extraction separation with the membrane system was studied in scenario 3, where a biostimulant with nitrogen and phosphorus concentrations similar to scenario 1 (0.22 % of N and 0.45 % of P) was obtained, although in a lower annual flow rate of 7,029 m³/year and higher carbon concentration due to solvent addition. These similar nitrogen concentrations between scenarios 1 and 3 were due to the use of the same separation system, with identical biomass concentrations (20 g/L). Nevertheless, 790 m³/year of biopesticide is also produced by extraction with solvent and posterior flash distillation (with 14.1 % of solvent concentration), which can be sold within a biorefinery process where a biomass is used to produce various types of bioproducts (Nagarajan et al., 2019). In the case of scenario 4, nitrogen concentration (0.85 %) was similar to that of scenario 2, in which a centrifuge was used in the harvesting and separation process and also, 165 m³/year of biopesticide were produced, with a solvent concentration of 15 %. In both scenarios, the amount of biopesticide active compounds solubilized was the same (10 % of biomass), but the final product was 4.8 times more diluted in scenario 3 (with membrane) than in scenario 4 (with centrifuge).

3.2. Techno-economic analysis

3.2.1. Investment cost (IC)

The IC was determined for the four scenarios based on the mass balances (Tables S.1, S.2, S.3, S.4), the equipment designed in each one to determine the TEC (Tables S.6, S.7, S.8, S.9) and then applied the Lang's Factors method to determine the fixed capital and the fixed capital per year (Table S.10). Differences were observed between scenarios 1 and 2 (Fig. 2), with higher TEC in the scenario 2 (466,232 €) than in scenario 1 (254,244 €). Cost increase was mainly due to the change in the algae harvesting system, since a centrifuge was used, which cost of 274,000 € was higher than the membrane system (26,156 €) (Fasaei et al., 2018). The same Lang factor was applied in both cases, so fixed capital was also higher in scenario 2 than in scenario 1, achieving 1,911,553 € and 1,042,401 € respectively.

Considering the different blocks depicted in Fig. 1, the TEC contribution of each block could be determined in both scenarios. In scenario 1, biostimulant production (which includes the reactor unit, final storage

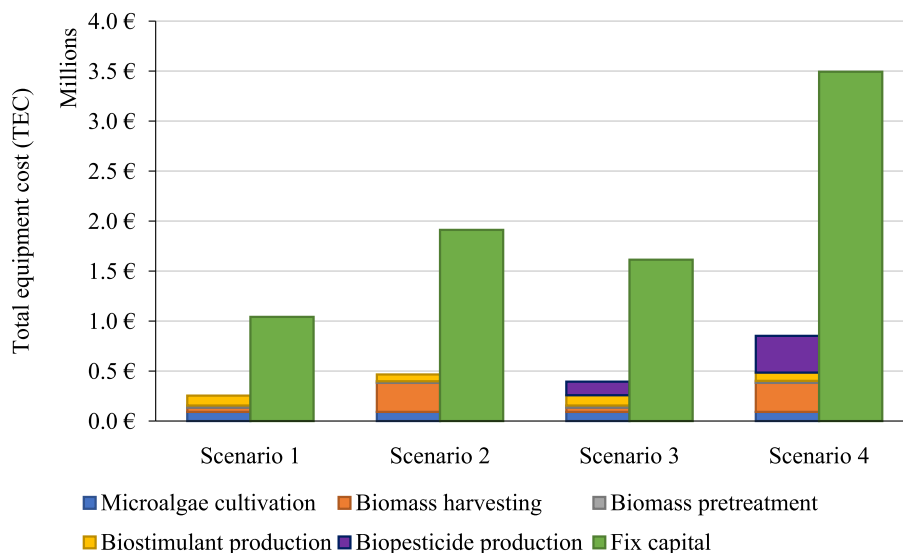


Fig. 2. Total equipment cost (TEC) and fix capital of the four scenarios.

tank, and pumps) contributed 39.0 % (99,160 €) followed by the microalgae cultivation block (which includes the medium preparation unit, the air blower, the CO₂ supply unit, the thin-layer, the harvest storage tank, and pumps) with 36.1 %, biomass harvesting with 16.7 % and biomass pretreatment with 8.2 %. The same cost was obtained in scenario 2 for the microalgae cultivation block and contributed 19.7 % to the TEC, and in this case biomass harvesting was the highest contributor (290,079 €) of the process with 62.2 %, followed by the biostimulant production (68,187 € and 14.6 % of contribution) and the biomass pretreatment (16,167 € and 3.5 % of contribution). The lower cost of these two blocks was due to the smaller size of the equipment because of the higher concentration of the streams obtained after centrifugation. As expected, these values were lower than those calculated by Acién et al. (2012), who performed an analysis to study the cultivation of pure microalgae in a tubular photobioreactor fed with synthetic media and harvested with a centrifuge to a concentration of 15 % of dry matter, obtaining 90.9 €/kg_{biomass} of TEC. This value is much higher than the TEC for cultivation and harvesting blocks obtained in this work (0.8 €/kg_{biomass} and 2.2 €/kg_{biomass} in scenarios 1 and 2 respectively). However, at this time, they were working in very different and non-optimized operational conditions and lower production scale. On the other hand, Romero-García et al. (2022) evaluated the production of a concentrated biofertilizer (6 %) from microalgal biomass produced in an urban wastewater plant with open photobioreactors. In this case, the process consisted of treatment of 412.5 T/year of algal biomass by high-pressure homogenization followed by enzymatic hydrolysis and TEC was 0.3 €/kg_{biomass}. This TEC was lower than our results for the biomass pretreatment and biostimulant production blocks (0.7 €/kg_{biomass} and 0.5 €/kg_{biomass} for scenario 1 and 2 respectively), but they analyzed a higher biostimulant production than this study.

As shown also in Fig. 2, high IC were also calculated in scenarios 3 (TEC = 393,697 € and fix capital = 1,614,160 €) and 4 (TEC = 852,212 € and fix capital = 3,494,069 €), where the process was designed for the simultaneous production of biostimulants and biopesticides. The quantity of equipment required in the biopesticide production (135,053 € for scenario 3 and 368,180 € for scenario 4) resulted in higher TEC compared to the scenarios 1 and 2. Regarding the costs distribution between the different stages of the process in scenarios 3 and 4, the largest contributor to the TEC in both scenarios (34.3 % and 43.2 % respectively) corresponded to the biopesticide production block, including the reactor unit, solvent extraction separation system, heat exchanger, flash distillation unit, final storage tank and pumps. However, in scenario 3, the next block of the process that contributed the most to the TEC was the biostimulant production with 26.3 % (103,560 €) while in the scenario 4 was the biomass harvesting

block with 34 % (290,079 € as in scenario 2). It is evidenced that the use of membranes allows to reduce the equipment cost of biomass harvesting and downstream separation. Finally, and as occurred in scenarios 1 and 2, the pretreatment of the biomass in scenarios 3 and 4 was the lowest contributor to the TEC (5.3 % and 2.4 % respectively).

3.2.2. Operational and maintenance costs

The OMC associated with each scenario were calculated based on the mass balances (Tables S.1, S.2, S.3, S.4), which allowed to determine the raw material (water, CO₂, enzymes, phosphate, and solvent) and inputs (electricity and heating) requirements in each process (Table S.11). As shown in the Table 4, OMC were different in each scenario, reaching values of 526,331 €/year, 429,548 €/year, 400,773 €/year and 380,714 €/year in scenarios 3, 4, 1 and 2 respectively. These differences were mainly due to the variation in the type of equipment, which require different quantities of raw materials and inputs as indicated in Table S.11, being higher in the scenario 3 than in the other three.

Fig. 3.A show the costs of raw materials required in all scenarios (€/year), and there were no significant differences between scenarios 1 and 2, since all their process blocks required a similar quantity of raw material (water and CO₂ for microalgae cultivation, enzymes, and phosphate for biostimulant production) whose contributions were ~5 %, ~32 %, ~41 % and ~20 % respectively. On the other hand, the integration of a biopesticide production block in scenarios 3 and 4 could slightly reduce the enzyme requirements in the production of biostimulants due to the reduction of the biomass flows within this block and spending 27,993 € on enzymes (36.5 % and 39 % of the total cost in scenarios 3 and 4 respectively). However, in these two scenarios, the additional use of solvent in the extraction of biopesticides had to be considered, being higher in

Table 4

Biopesticide and biostimulants production cost (€/m³) and production (m³/year) in each of the scenarios.

	Scenario 1	Scenario 2	Scenario 3	Scenario 4
IC (€)	1,063,997	1,951,154	1,647,600	3,566,456
OMC (€/year)	400,773	380,714	526,331	429,548
TAEC (€/year)	538,565	633,398	739,703	891,420
Biopesticide production (m ³ /year)	8,224	1,849	7,029	1,582
Biopesticide production cost (€/m ³)	65.5	342.6	65.5	342.6
Biostimulant production (m ³ /year)	–	–	790	165
Biostimulant production cost (€/m ³)	–	–	353.7	2,122.1

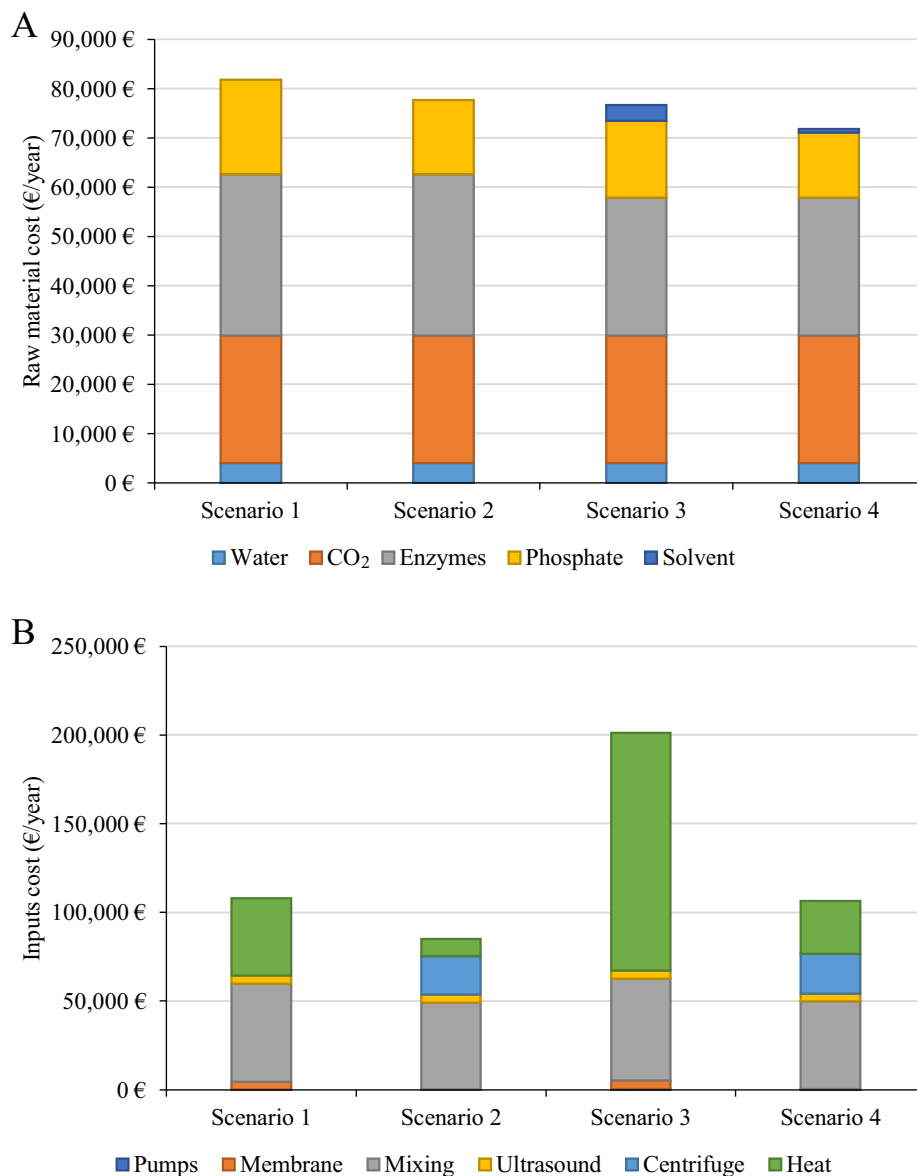


Fig. 3. A) Raw material costs (€/year); B) Inputs costs (€/year). *Pumps, membrane, mixing, ultrasound, and centrifuge inputs costs refers to electrical energy requirements.

scenario 3 with a contribution of 4.3 % than in scenario 4 (1.0 %) due to the more dilute stream in scenario 3 after membrane harvesting.

Considering the similarity in raw material costs, the differences in OMC between scenarios were mainly due to inputs cost (electricity and heat energy) as shown in Fig. 3.B. The high contribution of heat energy with 66.6 % in the scenario 3 was highlighting, compared to the other scenarios (40.3 % in scenario 1, 11.4 % in scenario 2 and 28.1 % in scenario 4). The low concentration of solids after membrane harvesting of biomass results in high heating requirements to remove solvent from the biopesticide product (Fig. 1.C), with a cost of 134,026 €/year. In this process, flash distillation is used to reach a solvent elimination of 94 % and to produce a biopesticide with low solvent concentration (14.1 %). Although in scenario 4 this purification process was also carried out, thanks to the higher concentration achieved with the centrifuges (see Fig. 1.D) and therefore small streams, the expenditure in heating energy was not so large, with 28.1 % of contribution to the total inputs cost. In Fig. 3.B, it was also observed that the energy requirements for the centrifuges (scenarios 2 and 4) was higher than in the membrane system (scenarios 1 and 3). The centrifuge of the algae harvesting block has an energy consumption of 1 kWh/m³ while the energy consumption of the membrane system employed was only 0.2 kWh/m³

(Zhao et al., 2023). Thus, the membrane system requires spending >4,000 €/year with a contribution to total costs of only 4 % and 2.5 % in scenarios 1 and 3, while the centrifuges made spend >20,000 €/year and contribute significantly to the total inputs cost (25.4 % in scenario 2 and 20.9 % in scenario 4).

Finally, based on the IC and OMC of each scenario (Tables S.10 and S.11), the TAEC was determined with Eq. (1). It also allowed estimated the production cost of the biostimulant and biopesticide produced to recover the total costs of their production (Eq. (2)). Results are presented on Table 4. The TAEC of scenarios 1 (538,565 €/year) and 2 (633,398 €/year) was comparable since both processes studied are similar with the only difference of the biomass harvesting method (a membrane system in the scenario 1 and a centrifuge in the scenario 2), which caused the cost increase in scenario 2 due to the higher cost of centrifuge than membrane (274,000 € vs 26,156 €). On the other hand, the TAEC of scenario 3 (739,703 €/year) and scenario 4 (891,420 €/year) was higher because the process is more complex and larger (where biostimulants and biopesticides are produced simultaneously) than scenarios 1 and 2, so it is consistent that the total production costs would increase. The use of membranes was beneficial to produce biostimulants but increased the operation costs

of the biopesticide production block, although it was also the best option to produce biopesticides by reducing investment costs (Table 4).

Because the amount of biostimulant produced among scenarios was different, it was estimated the biostimulant production cost per cubic meter produced. It should be noted that the use of a membrane system in scenario 1 for the harvesting process resulted in the lowest biostimulant production cost (65.5 €/m³) compared to the scenario 2 employed a centrifuge (342.6 €/m³). This cost divergence was mainly due to the difference in the concentration of biomass obtained after the harvesting process, which resulted in smaller and more concentrated streams in scenario 2 than in scenario 1. Finally, in scenarios 3 and 4 the production cost of the biostimulant was set at the same value as scenario 1 (since both processes used a membrane system for biomass harvesting) and scenario 2 (since both processes used a centrifuge for biomass harvesting), resulting in a biopesticide production cost of 353.7 and 2,122.1 €/m³ respectively. The difference in biopesticide flows (790 and 165 m³/year) was due to the different biomass harvesting methods and the further separation of solid and liquid phases after solvent extraction in scenarios 3 and 4. Scenario 3 provided a cheaper biopesticide than scenario 4, but also 4.8 times more diluted despite having solubilized the same amount of active ingredient (10 % of biomass) in the solvent extraction reactor. These biopesticide production costs are lower than those obtained by Kumar et al. (2019), who estimated the cost of production of biopesticides from starch industry wastewater by fermentation, resulting in 2,540 \$/m³. In general, the biorefinery concept allows reduce production costs, by using a more efficient and integrated process where several products are co-produced and a cheap raw material like piggyery wastewater.

3.3. Comparison with commercial products

Biostimulants are commonly used to enhance flowering, growth, and crop productivity (Amaya-Santos et al., 2022), which must contain N and P, the essential nutrients in the fertilizers for the proper growth of plants (Remya et al., 2021). For an adequate comparison, the produced biostimulants in this study must provide the same amount of nutrients as a commercial product. A comparison was made with a commercial fertilizer (Fercampo S.A., 2022) to evaluate the annual cost to fertilize one hectare of land (€/ha/year) based on the nutrient concentration (Table 3) to obtain the same N/P ratio and nutrient amount as the commercial product (Fig. 4).

As depicted in Fig. 4, the annual cost of fertilizing a hectare (ha) with the biostimulant produced from PWV in the four scenarios was lower than when the commercial product is used (383.1 €/ha-year). The use of

biostimulant is approximately 48.1 % cheaper in scenario 1 (where a membrane system was used for biomass harvesting) and 22.1 % in scenario 2 (where a centrifuge was employed) than the use of a commercial fertilizer. Due to the slight concentration of nutrients in the biostimulants obtained in scenarios 1 and 2, the amount needed to achieve the same nutrients supply in 1 ha as the commercial fertilizer was higher in both scenarios (3,036 and 872 L/ha-year) than commercial fertilizer (60 L/ha-year and 6.4 €/L) (Fercampo S.A., 2022). However, it should be noted that the commercial product must be applied diluted in irrigation water in any case. On the other hand, for scenarios 3 and 4, the biostimulant prices were fixed as in scenario 1 and 2, respectively. The small differences in annual costs between 1 and 3 and between 2 and 4 are due to the slightly different composition of the biostimulants obtained (Table 3). In these cases, the annual cost using the produced biostimulant was reduced by 45.1 % and 24.2 % respectively comparing with the commercial product.

Nevertheless, although the annual costs of fertilizer using bioproducts from PWV are lower than when commercial fertilizer is used, the high quantities needed could significantly increase distribution costs (Jin et al., 2022) and affect the feasibility of the process. Therefore, a study of the transportation costs of the bioproducts in scenarios 1 and 2 was carried out to determine the maximum distance (Fig. 5) at which the process is economically more viable than the commercial one (considering this constant over distances due to its small volume).

As shown in Fig. 5, the total cost varied according to the type of harvesting method. Using a membrane system (scenario 1), the maximum distance over which the process is economically more profitable commercially was 300 km, while using a centrifuge was 188 km, confirming that the use of membranes allows a more profitable process to be achieved by lowering costs even with larger volumes to be transported. So, for an economic feasible plant, it should be built close to the pig farms (to obtain the raw material) and at <300 km (scenario 1 using membrane for biomass harvesting) or 188 km (scenario 2 using a centrifuge for biomass harvesting) from the crops where the biostimulant would be used. However, it would be desirable to further optimize the process to obtain a more concentrated biostimulant to reduce the amount needed to obtain the same amount of nutrients as the commercial fertilizer.

Finally, considering the cost of commercial fertilizer (383.1 €/ha-year), it was possible to obtain the minimum capacity of the plant in each scenario to achieve a more economically viable process than the commercial one by recalculating equipment and operating costs on the basis of capacity. For scenario 1, the minimum plant capacity was ~12 m³/d, while in the scenario 2 was ~25 m³/d, which indicated that the use of membranes allowed

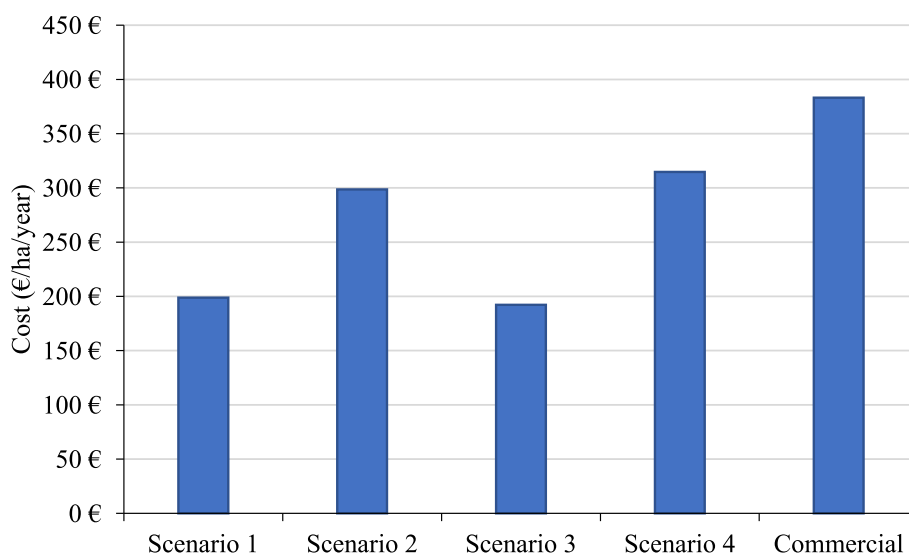


Fig. 4. Annual cost (€/ha/year) of the biostimulant in each scenario and comparison with commercial fertilizer.

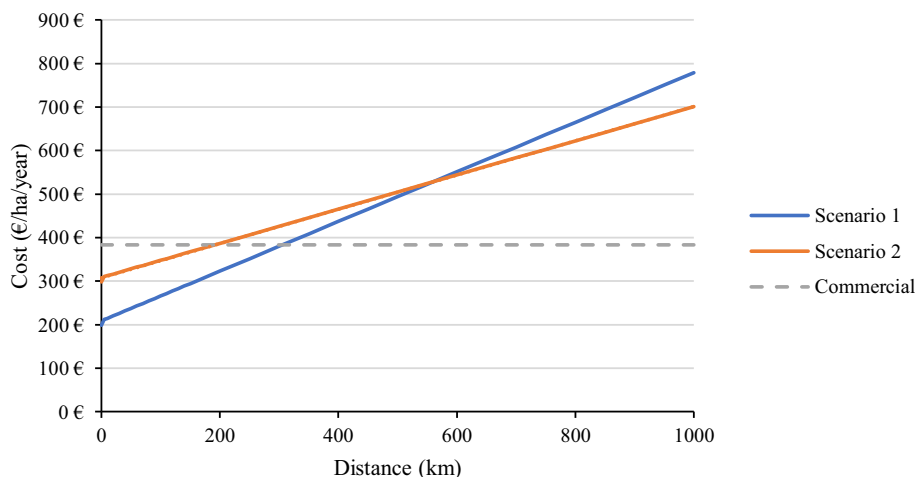


Fig. 5. Production plus transport costs of biostimulants (€/ha/year) as a function of distance (km) of scenarios 1 and 2 and comparison with the commercial product.

greater flexibility in plant capacity to achieve an economically sustainable process.

3.4. Sensitivity analysis

A sensitivity analysis was performed to analyze the effect of different operational parameters (PWW flow rate, electricity, and steam for heating cost) on the economic analysis and therefore, on the economic feasibility robustness of the designed process against changes in key variables.

The PWW flow had some impact on production cost for biostimulants and biopesticide in the designed plant as shown in Fig. 6. In the scenario 1, a 10 % reduction in the PWW flow increased the biostimulant production cost by 6 % (from 65.5 to 69.6 €/m³), while in the scenario 2 the same change in PWW flow increased the production cost by 7 % with a production of 1667 m³/year (from 342.6 to 368.0 €/m³). The same changes were observed with a 10 % increase in the PWW flow rate. This 10 % increase did not reduce the cost markedly, only 5 % in scenario 1 and 6 % in scenario 2, by increasing biostimulant production to 9,041 m³/year and 2,031 m³/year respectively. The same pattern was observed in scenarios 3 and 4, with PWW flow rate having an influence on biopesticide cost, since the decrease in flow increased the production cost of the biopesticide by 15 % and 21 % in both scenarios, respectively. It was therefore appreciated that the scenario where the change of flow can affect the most is the 4 (where a centrifuge was used for harvesting and separation and biopesticide is also produced).

Fig. 6 indicated that changes on the cost of electricity and steam also had some influence on the production cost of the bioproducts, although not to the same behavior as the PWW flow rate. A similar variation was observed in scenarios 1 and 2 when varying the price of electricity and steam. As electricity cost increased (to the maximum of 0.4 €/kWh observed on some days during the last trimester of 2022), the production cost of biostimulant, and therefore, its potential selling price, also increased in both scenarios by 9 % achieving 71.6 €/m³ and 374.6 €/m³ respectively, while increasing the steam cost up to 0.4 €/kWh, the production cost variation was very small (<3 %), since in both processes the heating energy requirements were small (only necessary in the hydrolysis reactor to maintain a temperature of 50 °C). However, due to the integration of a biopesticide purification process in scenario 3 (where more heating of the stream is necessary for the recovery of the volatile solvent than in scenarios 1 and 2) the influence of steam and electricity cost was moderate, with the final biopesticide cost varying by 18 % in both cases. Finally, in the scenario 4, the input that most influenced the price of the biopesticide was the cost of electricity which was able to modify the biopesticide production cost by 17 %. This was the largest variation by changing prices due mainly to the installation of two centrifuges with a high energy requirement (1 kWh/m³).

4. Conclusions

Several scenarios were studied in the production of two agricultural bioproducts (biostimulant and biopesticide) from the valorization of algal biomass grown in pig manure comparing two types of harvesting methods. The best harvesting method for biostimulant production was the membrane system which resulted in a production cost of 65.5 €/m³ by reducing investment and operating costs, while scenario 2 (using a centrifuge for harvesting) obtained about 4 times most concentrated biostimulant, although with a higher production cost (342.6 €/m³). Comparing with a commercial fertilizer, both scenarios obtained lower costs for the fertilization of 1 ha of land, being economically profitable at crop distances of <300 and 188 km respectively. Further research is needed to improve the process efficiency and produce more concentrated biostimulants using the membranes. The coupling of the production process of biopesticides increased the investment and operation costs due to the greater complexity of the processes, which suffered a greater influence with the changes in the prices of electricity in scenarios 3 and 4 and heat in scenario 3. In this case, it was also more beneficial to use a membrane by reducing investment costs but at the expense of obtaining a more dilute biopesticide. Future work may focus on the optimization of the solvent extraction process which has the greatest economic impact. Results from this study evidence that the transition to a circular economy valorizing PWW is not only an environmentally sustainable option but also an economically feasible one. In this context, policy makers should incentive and regulate the production and use of bioproducts from wastewater and other by-products. This study reveals that PWW should not be considered as a waste but as a valuable by-product with a potential market value. It has been also evidenced the importance of nearby crops to make economically feasible the production and use of bioproducts. This type of agriculture should be also promoted by policy makers to move from a linear economy to circular economy.

CRedit authorship contribution statement

Elena M. Rojo: experimental work, results analysis, drafting and writing - original draft. **María Molinos-Senante:** supervision, writing - review & editing. **A. Alejandro Filipigh:** experimental work, results analysis, and investigation. **Tomás Lafarga:** experimental work, results analysis, and investigation. **F. Gabriel Ación Fernández:** experimental work, results analysis, and investigation. **Silvia Bolado:** conceptualization, funding acquisition, supervision, writing - review & editing.

Data availability

The authors do not have permission to share data.

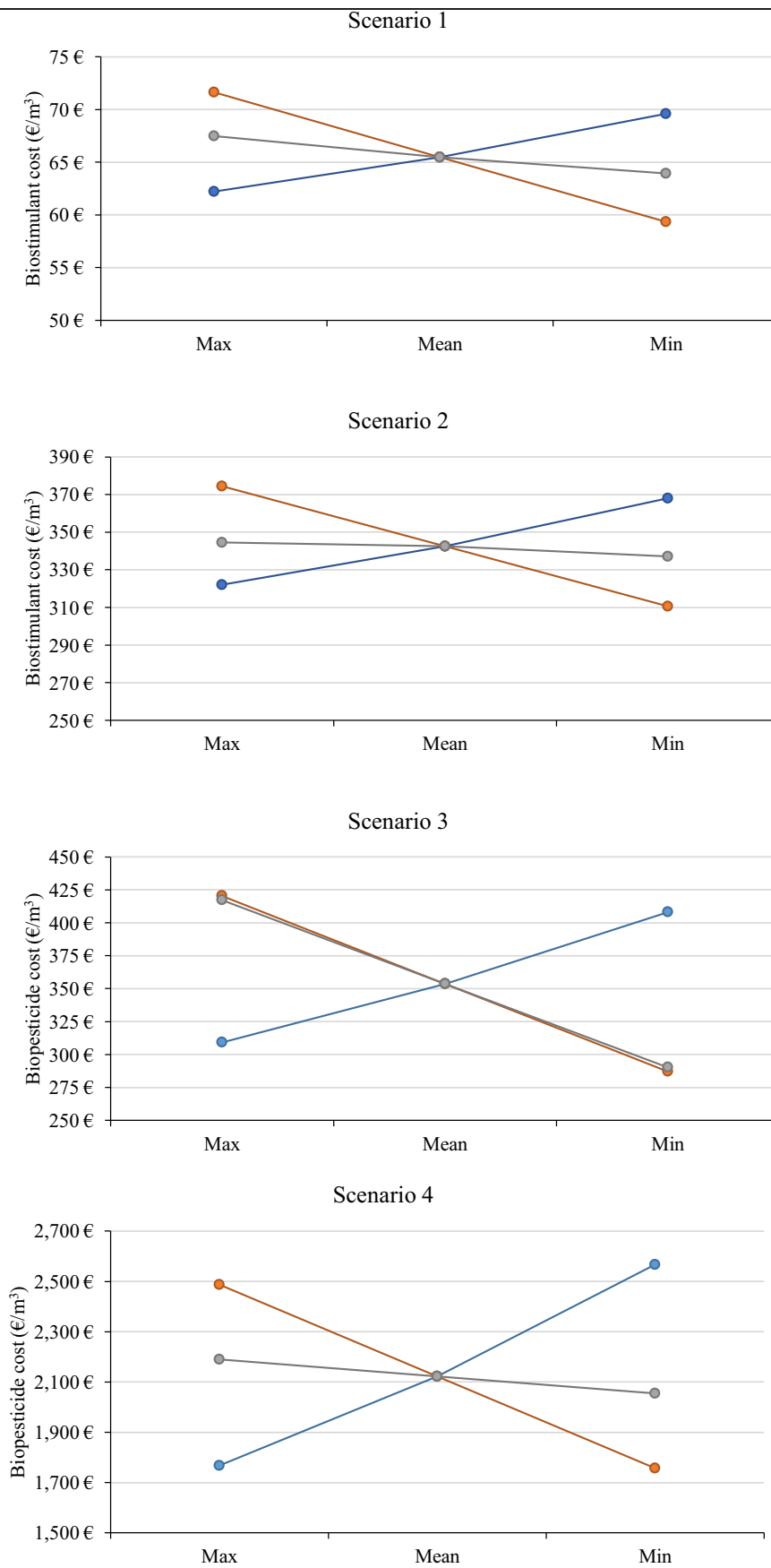


Fig. 6. Sensitivity analysis of biostimulant and biopesticide production costs (€/m³) towards the main operational parameters. Maximum, mean, and minimum values were established in Table 2. PWW (blue line), electricity cost (orange line), steam cost (grey line).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.164159>.

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