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LCA of Zero Valent Iron Nanoparticles Encapsulated in Algal Biomass for Polishing Treated Effluents

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***Abstract* – Research data produced within the CARIPLO IMAP and Perform Water 2030 projects were processed using the *SimaPro* software to carry out the Life Cycle Assessment according to ISO 14040-44 of an innovative process of treated effluents' polishing. The study aims to evaluate the integration of a microalgae culture as a side-stream process into the baseline layout of a wastewater treatment plant to remove nitrogen from the supernatant of sludge centrifugation from an environmental perspective. In particular, the investigated system focuses on using the algal biomass produced as an organic matrix for encapsulating zero-valent iron nanoparticles to be used for the final refinement of the effluent. Zero-valent iron (ZVI) is a reactive metal and an effective reducing agent. It can be used to remove organic and inorganic pollutants (e.g., chlorinated organics, pharmaceuticals, metals, textile dyestuffs). The encapsulation of ZVI by hydrothermal carbonization (HTC) in a carbonaceous matrix allows for overcoming the problems related to its lack of stability, easy aggregation, and difficulty in separating the ZVI nanoparticles from the treated solution. The case study refers to Bresso wastewater treatment plant (Milan province, Northern Italy). The environmental performances of the study were assessed following the Life Cycle Impact Assessment methods IMPACT 2002+. According to the results, the new process integration does not affect the environmental performance of the WWTP, still implying a significant improvement in the removal of metals and micropollutants. In fact, due to the ability of ZVI nanoparticles to remove organic and inorganic pollutants, the outflowing load will be significantly reduced, which will improve the environmental performance of the entire Bresso wastewater treatment plant.**

***Keywords* – Hydrothermal carbonization; metals; microalgae; nitrogen removal; organic micropollutants; wastewater treatment plant**

1. INTRODUCTION

Microalgal-based wastewater and other side-waste stream treatments (i.e. digestate) can remove nutrients and other pollutants [1]–[5]. Thus, due to the content of valuable molecules, microalgal biomass can usefully create an interface towards different added-value product extraction processes [6], [7]. However, not all valorization pathways could be exploited for microalgal biomass grown in wastewater or municipal digestates.

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Several studies emphasize the need for advanced sustainable technologies to remove emerging contaminants in wastewater treatment plants where, as it is well known, the removal efficiency for those kinds of substance is variable and often inadequate [8]–[10].

Within this background, the use of zero-valent iron (ZVI) for polishing organic and inorganic micropollutants and metals represents an innovative approach [11]–[15]. In fact, the ZVI is acting as the electron donor in Advanced Oxidation Processes [16], [17] or as a reductive agent [18]. Encapsulating ZVI in organic matrices, like microalgae, could overcome practical problems within this application, such as aggregation, lack of stability, and difficult separation from the treated solution [11].

The study of Arvaniti *et al.* [18] highlights that coated or encapsulated ZVI nanoparticles (nZVI) show significant removals of perfluorinated compounds (PFC) (38–96 %) by using Mg-aminoclay coated nanoscale zero-valent iron (starting pH = 3.0). Furthermore, the same study underlines a maximum removal efficiency for the perfluorooctanoic acid (PFOA), followed by the perfluorononanoic acid (PFNA), the perfluorooctane sulfonate (PFOS), and the perfluorodecanoic acid (PFDA). The reason was attributed both to sorption and degradation.

nZVI particles encapsulated in microscale carbon spheres (6−8 μm), via an *in situ* formation through hydrothermal carbonization (HTC) from an organic compound, have the excellent chemical reducing capability of nZVI, and a high sorption capacity, facilitated by the carbon substrate. HTC is a thermal treatment of an aqueous solution or dispersion of a carbon-containing organic material at moderate temperatures and under pressure, which produces a carbon-rich black solid as an insoluble product [19]. The incorporation of nZVI into solid particles results in its easy separation from aqueous systems avoiding aggregation of nZVI. Encouraging results for metal removal (Zn, Cu, Ni, Cd, Cr) have been obtained at a lab-scale by Bonaiti *et al.* [15] using clarified olive mill waste (OMW) as the source of carbon to produce carbon encapsulated nZVI by HTC.

Within the context, microalgal biomass has been proposed as a possible matrix for encapsulating nZVI [20], opening an alternative use of the algae biomass with a high added value product. For a preliminary evaluation of the environmental sustainability of a potential commercial technology using microalgae for encapsulating nZVI, a Life Cycle Assessment (LCA) study was performed based on the main findings from a pilot project.

2. RESEARCH METHODOLOGY

This research aims to provide insight into the environmental burdens of a polishing treatment of effluents from a wastewater treatment plant (WWTP) using nZVI encapsulated in microalgal biomass. The microalgal biomass is derived from an existing raceway pilot plant located in Bresso WWTP (Milano, Italy), operated since 2017. The pilot plant was designed to test a microalgae-based process to treat the liquid separated from the digestate (centrate) and works side-stream [4], [21].

The method used for the data collection and analysis is the LCA approach, a consistent yet quantitative method for a 'cradle-to-grave' evaluation according to the Standards ISO 14040, ISO 14044 [22], [23], and in line with the Product Environmental Footprint Guidelines [24].

The LCA methodology is based on a systemic evaluation of the environmental burdens of products or services towards potential impact categories implementing consistent mass and energy balances [25], [26].

The *SimaPro* software, version 9.1©, was used. Specifically, the IMPACT 2002+ method was selected to evaluate the environmental performances of the investigated system [27].

3. THE LCA CASE STUDY

The case study of this research is carried out using the baseline data reported by Tua *et al.* for Bresso WWTP and the side-stream microalgae process [21] but also the following upgrading (i.e., biomethane upgrading in the sludge line and decrease of Hydraulic Retention Time (HRT) in the pilot raceway). The present paper aims to evaluate the potential benefit of adding to the algae raceway module the valorization of microalgal biomass by processing into encapsulated nZVI. nZVI can be used to remove organic micropollutants and heavy metals from the WWTP effluent. The intention is to explore the potential benefits and drawbacks of such an innovative polishing method. The encapsulation is supposed to be carried out by hydrothermal carbonization (HTC) with the addition of an aqueous solution of iron (III) nitrate.

Bresso WWTP receives about 19.6 million m^3/year of wastewater from 220 000 Population Equivalents (PE). The flowsheet includes a water line, consisting of mechanical treatments (screening, sand, and oil removal), primary settling, activated sludge with pre-denitrification and nitrification, secondary settling, tertiary treatment by coagulation-filtration and disinfection by UV, and a sludge line with two anaerobic mesophilic (i.e., 35 °C) digesters. Two Combined Heat and Power (CHP) units exploit the biogas and, recently, a biogas upgrading system has been installed to separate methane from CO_2 and other gases. The separation of the solid and liquid phases is carried out by centrifugation.

3.1. Goal and scope

The study's first goal was to assess the possible improvements in the WWTP due to the introduction of an innovative process for refining treated effluents combined with a side-stream, microalgae-based process to treat the centrate. The technological scheme involves two main solutions: the integration of the microalgae unit in the baseline layout of Bresso WWTP for the removal of nitrogen from the centrate, and the valorisation of the produced microalgal biomass as an organic matrix for encapsulating zero-valent iron nanoparticles to be used for the final polishing of the WWTP effluent. This technological scheme provides an innovative solution to the increase of the nitrogen load entering the WWTP, caused by the conventional recirculation of the centrate to the water line and a refinement of the final effluents to effectively remove organic micropollutants and heavy metals.

The comparison of the alternative treatment layouts was addressed by selecting as Functional Unit (FU), the hourly flow rate of the wastewater treated by Bresso WWTP, equal to 2238.81 m^3/h. A technical life of 20 years was assumed.

The study aims to compare the baseline scenario proposed in the work of Tua *et al.* [21], as an existing technological layout (i.e. *Baseline system* in Fig. 1), with a second scenario integrating a side-stream algal process and an HTC unit to produce nanoparticles to polish tertiary effluents (i.e. *Foreseen system* in Fig. 1). It must be clarified that this study's main findings rely only on the differences of the second scenario with respect to the baseline scenario. In other words, the results further presented show the net impact considering the benefits, including the additional processes of the HTC and the production of nZVI.

In detail, the system boundaries, set and reported in Fig. 1, for the scenario implementing nZVI includes:

- the baseline scenario;
- the construction of the raceway pond for the microalgal-based process to treat the centrate, including excavation, the main components of the plant, and the land occupation;

– the installation of the HTC reactor and the associated equipments;
– the electric power demand for the HTC and the nZVI units;
– the benefits related to the variation of the load of inorganic and organic pollutants outflowing Bresso WWTP;
– the benefits from the valorization of microalgal biomass to produce nZVI a substitute of activated carbon to remove both organic and inorganic pollutants such as metals.

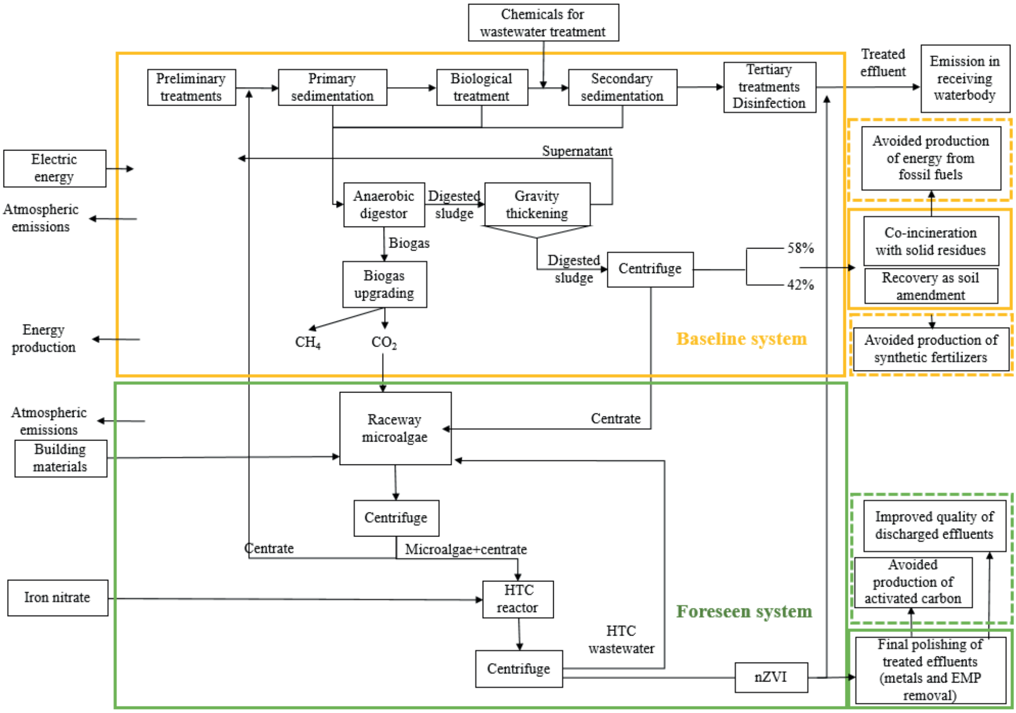

Fig. 1. Layout of the LCA's system boundaries.

The description of the existing WWTP system and the microalgal raceway pond, as well as the process efficiencies, including the removal of pollutants by microalgae, was based on data from Bresso WWTP, from published data [4], [21] and from lab-scale testing at the Department of Earth and Environmental Sciences at the University of Milano Bicocca (DISAT). Secondary data were gathered from scientific and technical literature. *Ecoinvent 3.6* database [28], was used to model the background processes mostly addressed to compounds (e.g. chemicals) and energy flows.

The impact description and assessment were carried out according to the IMPACT 2002+ method [27] in line with the ILCD approach [29]–[36]. More specifically IMPACT 2002+ presents an implementation working both at midpoint and damage mid-point impact categories as it is possible to see in Fig. 2.

The term 'midpoint' expresses the fact that this point is located somewhere on an intermediate position between the LCI results and the damage on the impact pathway. In consequence, a further step may allocate these midpoint categories to one or more damage categories, the latter representing quality changes of the environment. A damage indicator result is the quantified representation of this quality change and calculated by multiplying the damage factor with the inventory data.

Fig. 2 shows the overall scheme of the IMPACT 2002+ framework, linking all types of LCI results via several midpoint categories represented with several indicators, namely: Human toxicity as carcinogens and non-carcinogens (kg of C_2H_3Cl equivalent), Respiratory effects (kg of PM 2.5 equivalent), Ionizing radiation (kg of Bq C-14 equivalent), Ozone layer depletion (kg of CFC-11 equivalent), Photochemical oxidation (kg C_2H_4 equivalent), Aquatic ecotoxicity (kg of Triethylene glycol in water), Terrestrial ecotoxicity (kg of Triethylene glycol in soil), Aquatic acidification (kg of SO_2 equivalent), Aquatic eutrophication (kg of PO_4^{3-} into water equivalent), Terrestrial acidification/nutrification (kg of SO_2 equivalent), Land occupation (m^2 of arable land), Global warming (t CO_2 equivalent), Non-renewable energy (GJ primary), Mineral extraction (GJ surplus).

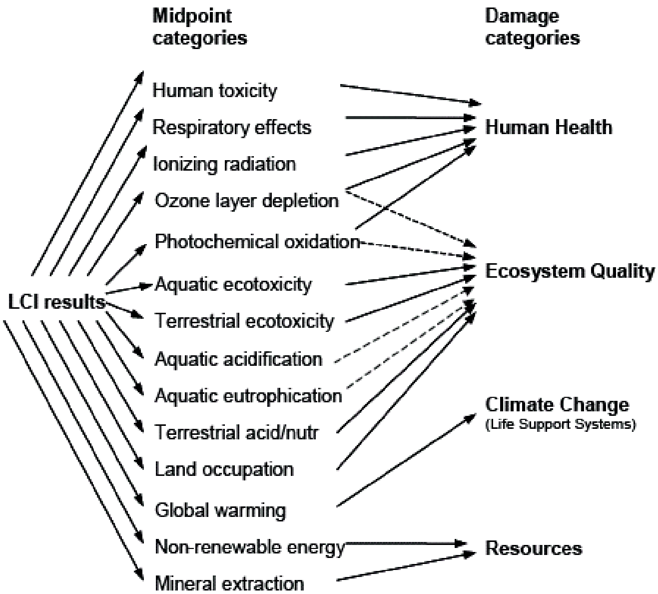

Fig. 2. IMPACT 2002+ scheme [29].

The four damage categories are: human health (expressed as DALY as DALY= Disability-Adjusted Life Years), ecosystem quality (expressed as PDF m^{-2} $year^{-1}$, where PDF is Potentially Disappeared Fraction of species), climate change (kg CO_2 into air equivalent), and resources (MJ). An arrow in Fig. 2 shows that an impact pathway is known and quantitatively modelled. The dotted arrows refer to impact pathways between midpoint and damage levels that are assumed to exist, but that are not modelled quantitatively due to missing knowledge or other reasons (i.e. in development or double counting).

More information on the IMPACT 2002+ framework can be found in Jolliet *et al.* [37], where the normalization factors to the ecological scores expressed in *Pt* (as average impact per person per year) are reported.

3.2. Life Cycle Inventory analysis

The data concerning the baseline flowsheet were based on the study of Tua *et al.* [21] and on the updated parameters deriving from the WWTP upgrading and the modified operation of the pilot algal raceway.

Table 1 reports the inventory data for the algal cultivation system. For all parameters, a safety factor of 1.2 has then been applied. The production process of the liner, in EPDM rubber, was modelled according to the *Ecoinvent 3.6* database inventory for the European context. The life cycle of the paddlewheel was not modelled because of lacking inventory data, but it is recommended to avoid the use of fiberglass reinforced plastic materials in their construction, due to the high impact of their production on human health [38]. In the same way, it is recommended to avoid the use of concrete for the construction of the algal unit, in order to limit environmental impact [38], [39].

With reference to the system boundaries of Fig. 1, in this study, the use of the CO_2 from the biogas upgrading within the microalgae ponds was considered as an environmental benefit. A difference from the baseline data from Tua *et al.* study [21] is the lower emission of NH_3 resulting from recent experimental data obtained by DICA (Politecnico di Milano). Moreover, the HRT in the algal raceway was set equal at 7 days.

TABLE 1. INVENTORY DATA FOR THE ALGAL CULTIVATION UNIT

Reactor	Excavated pond, lined and mixed by paddle wheel
Lining material	EPDM, 1250 g/m^2 weight, 1 mm thick, 39 g/FU
Area	0.1 m^2/PE, 2.2 ha/ FU
Life cycle	20 years
Working days per year	275
Average depth	10 cm
Inflow	Centrate: 4.48 m^3/FU
HRT	7 days
Excavation volume	2.58 m^3/FU
Land occupation	10.31 m^2/FU
Microalgal strains	*Chlorella* spp., *Scenedesmus* spp.

Table 2 refers to the HTC plant. In the absence of real or experimental data, the information relating to the HTC reactor was based on preliminary results from the Laboratory of Environmental Physical Chemistry at DISAT and scientific literature. An HTC reactor of similar size was used as a reference model [40] to quantify the amount of material required for the reactor's construction. The needed amount of iron nitrate to produce nZVI was calculated assuming an optimal ratio between iron and carbon of the algal biomass of 0.2 and an average content of C in the algal biomass of 40 %. It was assumed that at the end of the HTC process, the zero-valent iron nanoparticles are recovered from the wastewater by centrifuging. The wastewater extracted from the centrifuge is used to feed microalgae, by adding it to centrate; it is thus possible to avoid the costs and impacts resulting from its disposal.

TABLE 2. INVENTORY DATA FOR HTC REACTOR

Materials for HTC reactor	Hot rolled steel sheet: 28.13 g/FU, Stainless steel hot rolled coil: 59.92 g/FU
Iron nitrate	2.60 kg/FU
Transport	0.039 tkm
Inflow	2.87 m^3/FU
Production of nZVI	51.61 kg/FU

The variation of the electricity request of Bresso WWTP in the new flowsheet, integrating algal cultivation and HTC (see Table 3), was modelled according to the Italian electricity mix. The following aspects were taken into consideration in the analysis.

For the sludge line, the electricity demand from the two centrifuges, equal to 1.18 kWh/FU, was calculated based on the consumption of the centrifuge operating at the Bresso plant for sludge dewatering (i.e. 0.25 kWh/FU) with a conversion factor of 0.213 considering the variation of dry matter content of sludge after centrifuging (from 3 % to 24 %). The same approach was used to estimate the energy demand to centrifuge the algal biomass outflowing the raceway. Thus, the energy demand was calculated based on the need to increase the solid concentration from 0.8 g/L (outflowing the raceway) to the necessary concentration inside the HTC reactor (30 g/L) demand.

When integrating the *foreseen system*, the electricity demand from the water line was calculated by subtracting the savings due to the decrease of NH_4-N load entering the WWTP with the re-circulated centrate, to the baseline demand (estimated as 2.4 kWh/kg N), according to [21]. The amount of NH_4-N removed by the algal treatment was quantified according to [4], but the amount lost by stripping was adjusted on the basis of more recent experimental data showing that, on an annual scale, 11 % of the removed N was stripped as NH_3. For the algal mixing system, using mechanical paddlewheels, a specific power consumption of 2 W/m^3 of treated water was drawn from [41] and applied to a 10 cm water depth and 11 000 m^2 water surface to be mixed 275 days per year, for 24 hours a day.

The demand for pumping was estimated considering several aspects:

- the supply of centrate to the algal pond, the injection of CO_2 in the algal pond;
- the pumping of the algal suspension from the pond to the centrifuge;
- the injection of the algal biomass from the centrifuge to the HTC reactor and the return of the supernatant to the algal pond;
- the general pumping system;
- the working time and the specific energy consumption.

The electricity demand of HTC reactor was estimated according to Roy *et al.* [40].

TABLE 3. THE ELECTRICITY DEMAND IN THE VARIOUS SECTIONS OF THE NEW FLOWSHEET, INTEGRATING ALGAL CULTIVATION AND HTC

Electricity demand from the WWTP sludge line	35.01 kWh/FU
Electricity demand from the WWTP water line	222.03 kWh/FU
Electricity demand for the algal unit (paddlewheel)	0.99 kWh/FU
Electricity demand for pumping	0.81 kWh/FU
Electricity demand for algal centrifuging	1.18 kWh/FU
Electricity demand for HTC	1.37 kWh/FU

The variation of air emissions between the integrated and the baseline system was calculated by combining the following aspects (Table 4):

- the emissions from the CHP unit;
- the microalgal uptake of 2.79 kg CO_2/FU, provided by the biogas upgrading system; the ammonia stripping from the algal pond (0.10 kg/FU);
- the emission of CO_2 by microalgal respiration at night (1.29 kg/FU), calculated considering also the amounts of CO_2 introduced into the raceway (4.09 kg/FU) and of CO_2 absorbed by the microalgae (2.89 kg/FU) as well as the algal biomass concentration in the raceway;
- the air emission from the HTC plant: a gas is emitted composed of 93.6 % CO_2, 5.1 % CO and the remaining 1.3 % of other gases including H_2, CH_4, ethane and propylene, according to Roy *et al.* [40].

The removal of heavy metals in the water line was considered, according to [21]. The removed amount was multiplied by a corrective factor of 2 to account for the further removal deriving from the use of nZVI in the tertiary treatment (Table 5).

The potential removal by nZVI is actually much higher, but the amount produced in the reference conditions would not be enough to treat the whole effluent flow, so a precautionary estimate was made.

TABLE 4. VARIATION OF THE DIRECT AIR EMISSIONS IN THE WWTP

Parameter	Total emission/FU	Avoided emissions/FU
NO	294.12 g	
SO_2	31.36 g	
CO_2	31.64 kg	2.89 kg
NH_3	0.57 kg	–
CO_2	9.938 g	–
CO	0.541 g	–
H_2	0.032 g/FU	–
CH_4	0.035 g/FU	–
Ethane	0.035 g/FU	–
Propylene	0.035 g/FU	–

Due to both microalgae [5], [42] and the use of nZVI in the tertiary treatment, the removal of emerging contaminants was not calculated but can be expected.

TABLE 5. REMOVAL OF HEAVY METALS IN THE FINAL EFFLUENT

Metal	Amount removed by microalgae, g/FU	Amount removed by nZVI, g/FU
Copper (Cu)	1.11	2.23
Zinc (Zn)	5.51	11.02
Lead (Pb)	0.11	0.22
Nickel (Ni)	0.59	1.19

4. LIFE CYCLE IMPACT ASSESSMENT: RESULTS AND ANALYSIS

Fig. 3 compares the impacts deriving from the existing Bresso WWTP (*baseline system*) and the *foreseen system*, including the treatment of centrate by microalgae, the production of nZVI from the produced microalgal biomass and the use of nZVI in the tertiary treatment of the water line. The results show a clear improvement in the environmental impact from the *baseline* to the *foreseen system*, despite the increase in Terrestrial Eutrophication, due to the emission of nitrogen oxides. The main cause of the improvement is the removal of heavy metals and other contaminants, more efficient when using nZVI, able to remove both, than activated carbon, leading to a strong decrease in Freshwater Ecotoxicity and in Human toxicity, non-carcinogens as well.

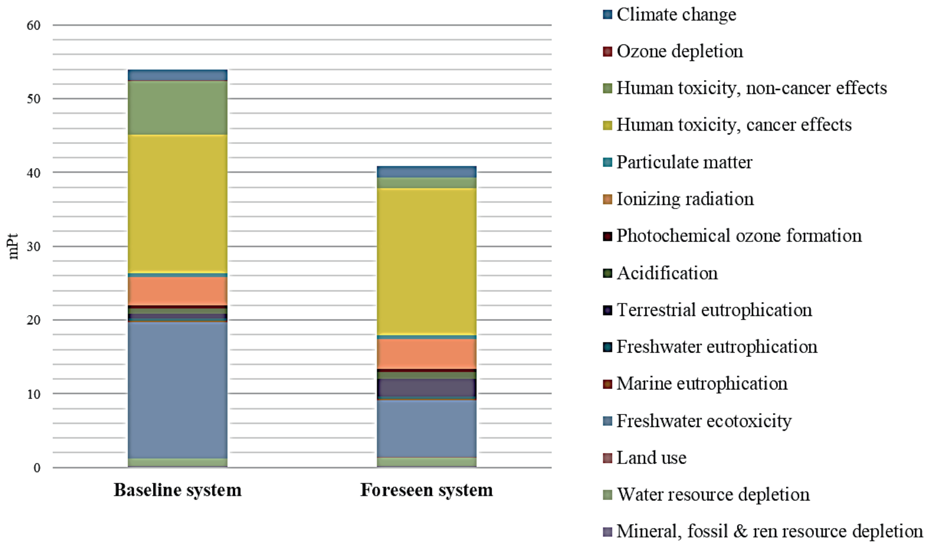

Fig. 3. Comparison between the impacts deriving from the baseline and the *foreseen system.*

Human toxicity, cancer effect, represents the most impactful category for both scenarios. This is evaluated on the basis of the environmental distribution of substances and on the exposure pathways by inhalation, ingestion, and skin exposure. The Human Damage factors for carcinogens and non-carcinogens evaluate the intake fractions, estimates of dose-response, as well as severities [27]. Human toxicity represents all effects on human health, except for respiratory effects caused by inorganics, ionizing radiation effects, ozone layer depletion effects and photochemical oxidation effects that are considered separately. These are determined with the IMPACT 2002+ approach by modelling risks and potential impacts for several thousand chemicals. That means that for the investigated scenarios, the overall toxicological risk is potentially high as well as the potential impacts associated with the chemicals emitted into the environment mainly in terms of Ethane and Propylene, as reported in Table 4.

Fig. 4 summarizes the impacts of the different sections of the *foreseen system*. The effect of the use of nZVI involves, of course, the greatest factor of improvement, and is especially related to the decrease of the impacts concerning ecotoxicity and human toxicity. In the case of the algal raceway, the most important impacts derive from the emission of NH_3, contributing to terrestrial eutrophication, and, to a lower extent, from energy consumption, involving the emission of pollutants affecting Freshwater ecotoxicity. For HTC, the main impact source is the liquid effluent from the process which could have negative effects in terms of Freshwater ecotoxicity [43]. The second important item is the energy consumption whose impacts affect Human toxicity, and once more Freshwater toxicity. Negative effects due to the process can also be observed for Climate change.

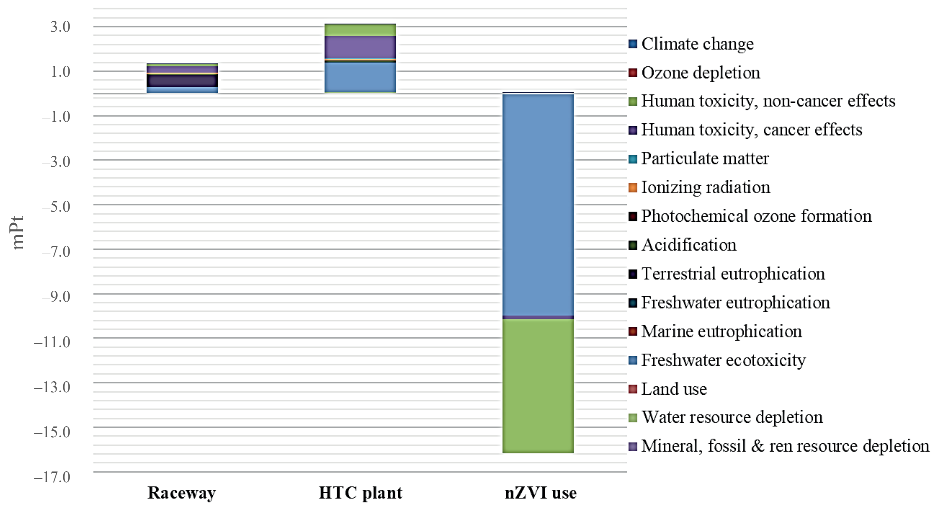

Fig. 4. Contribution of the different sections to the overall impact of the *foreseen system.*

Sensitivity analyses were performed to test the effects of the variation of: algal productivity, energy consumption for the pumping system, performance of the HTC reactor and energy consumption by HTC reactor. Results are reported in Fig. 5 and show that an optimized scenario would involve a higher algal productivity and a better performance of HTC reactors, while no variation could be expected modifying the values of energy consumption, both for pumping and for HTC process. Interestingly, for both algal productivity and HTC performances, variations in the order of 10 %, which are not so unlikely to be obtained, seem enough to cause significant improvements.

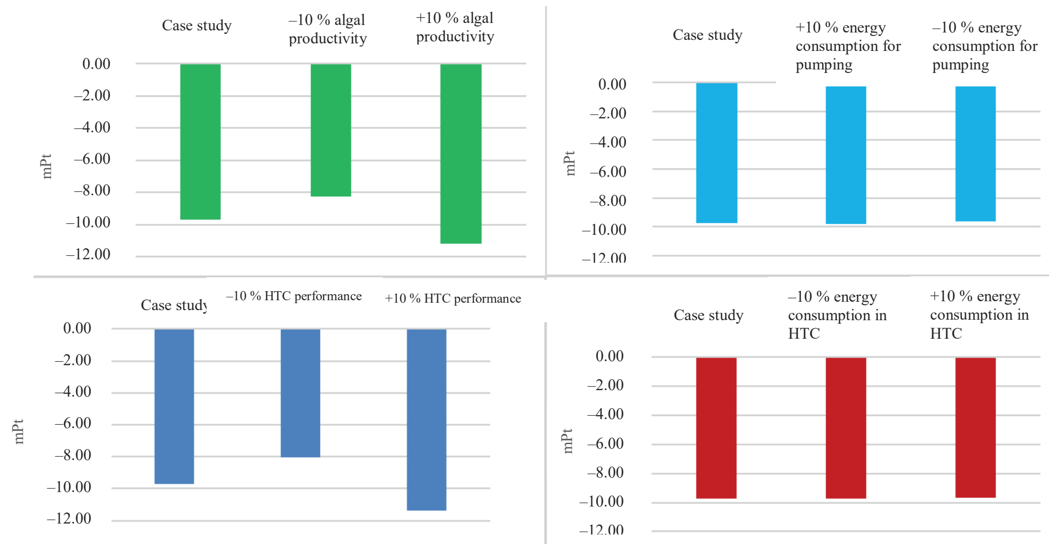

Fig. 5. Results of the sensitivity analyses carried out considering 10 % positive and negative variations in algal productivity, energy consumption for pumping, HTC performance and energy consumption in HTC.

5. Conclusions

The LCA aimed to evaluate a new wastewater treatment scheme including the use of microalgae to remove nitrogen from the centrate, the valorization of microalgal biomass as a carbon matrix to encapsulate nZVI by HTC synthesis, and the use of the encapsulated nZVI for the final polishing of the effluent from a municipal WWTP.

The assessment confirms that one of the most critical points about microalgal-based treatment of wastewaters and centrates is the final fate of the produced biomass. The *foreseen system* analyzed in the present paper includes not only an interesting process to valorize the biomass, but also a way to add positive impacts to the system in its own environment, that is the removal of residual pollutants from the treated effluent and the improvement of impacts on surface waters. Moreover, the potential ecotoxicity of the HTC effluent, which is a critical aspect, could be strongly decreased by adding the effluent from HTC to centrate to feed the algal raceway. The positive effects could increase if a greater amount of nZVI could be produced, and this could be obtained by increasing algal productivity. Another possibility could be the increase of the size of the algal unit, which could be fed on a mixture of inflowing wastewater and centrate, but this would involve further impacts, which should be analyzed in a different LCA.

As expected, the impacts decrease with increasing efficiency of the system, both for algal productivity and for HTC process, as confirmed by the sensitivity analyses. One drawback is still energy and, especially, the emissions that the use of energy still involves, but this seems to be less important in the presented case study, while it is still a major issue from a global sustainability perspective.

Acknowledgement

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