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Life Cycle Assessment of emerging environmental technologies in the early stage of development: a case study on nanostructured materials

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Abstract

The use of nanostructured materials has been recently proposed in the field of environmental nanoremediation. This approach consists in using nano- materials not directly, but as building blocks for the design of nano-porous micro-dimensional systems, overcoming the eco- and health-toxicology risks generally associated with the use of nano-sized technologies. Herein we report the use of life cycle assessment (LCA) as an eco-design tool for optimizing the production of cellulose nanosponges (CNS), nanostructured materials recently developed for water remediation purposes. LCA was applied from the acquisition of raw materials to the synthesis of CNS (from cradle to gate), considering three production systems, from the lab-level to a modelled scale-up system. The

lab-scale LCA identified the main environmental hotspots, namely the energy consuming steps and the final purification of the material (washing step). In a second lab-scale production, an improvement action could be implemented, switching the washing solvent from methanol to water and decreasing the washing temperature. A second LCA showed a reduced contribution to the impacts from the materials, while the global impacts remained within the same order of magnitude. A simulated scale-up of the process allowed to optimize the energy-consuming steps and the water consumption, through internal recycling. A third LCA assessed the resulting benefits and a decrease in the global impacts by two orders of magnitude. Our study contributes to the discussion of LCA community, providing a focus on the importance of scaling up of emerging technologies, namely nanostructured porous materials, highlighting the benefits of a LCA based approach since the very beginning of product design (eco-design).

KEYWORDS: Life cycle assessment; scale-up; eco-design; cellulose nanosponges; prospective LCA, nanotechnologies.

<heading level 1> Introduction

Nanomaterials and nanoparticles have received increasing attention among scholars, practitioners (such as manufacturing firms and consultants) and policy makers. The European Commission has classified nanomaterials as a “key enabling technology”, that is one of those technologies which provide the basis for innovation of new products and services with enhanced commercial and social value, and which play an important role in the development of sustainable competitiveness and growth (European Commission, 2004).

Since 2005, in its report “Nanosciences and nanotechnologies: An action plan for Europe 2005-2009”, the European Commission highlighted that “health safety and environmental risks that may be associated with products and application of nanomaterials need to be addressed upfront and throughout their life cycle” (European Commission 2005, pp 3).

The important role of life cycle assessment (LCA) in the evaluation of the environmental impacts of emerging technologies, since the early development phases, has been recognized across several different sectors (e.g., nanomaterials, energy technologies, biomaterials etc.). In particular, LCA has been used not only to compare innovative technologies to commercial ones, but also to identify their environmental hotspots and drive improvement actions, following an eco-design approach. Eco-design can be defined as “the integration of environmental aspects into product design with the aim of improving the environmental performance of the product throughout its whole life cycle” (European Commission, 2009 pp. 17).

However, grounding on the analysis of a number of case studies available in the literature, several methodological issues connected to the use of LCA as development tool of emerging technologies have been identified.

Hetherington et al. (2014) summarized the main drawbacks, providing useful guidelines to overcome them. At an early stage, they are mainly related to the difficulties to compare them with existing technologies, the scaling up, the scarce data availability, and the data uncertainty. Cucurachi et al. (2018) identified as a criticism the definition of the functionality of the innovative product, which is essential to correctly define the functional unit in the LCA study. Also impact assessment issues appear relevant, as they regard specific flows, which are not yet classified and characterized, and therefore cannot be accounted for in the life cycle impact assessment phase. Recently, Arvidsson et al. (2018) proposed the term ‘prospective LCA’ for defining the analysis used to assess and guide the development of emerging technologies. In order to perform correctly this type of approach, the authors recommend particular attention to data availability and quality.

Several contributions report the use of a life cycle approach to support the eco-design of nanomaterials (Wardak, 2008; Bauer et al., 2008; Tsuzuki, 2014). For instance, Eckelman et al. (2008) focused on the improvement of the efficiency of manufacturing processes (in terms of

energy and resources consumption) in all stages of the life cycle, while Karn (2008) also focused on the choice of non-toxic reagents.

Tsutzuki (2014) recommended the application of LCA to assess and check that the production synthetic strategies used in nanotechnology avoid the use of raw materials containing scarce resources or hazardous substances, and that they apply production methods with low energy and resources consumption (e.g., water).

Nano-manufacturing processes have in fact intrinsic features that often make them energy and resource intensive (Sengul et al. 2008; Dhingra et al. 2010). These include low process yields, intensive purification procedures, use of toxic, acidic or basic chemicals and organic solvents, vacuum process steps and, in most cases, the use of rare starting materials.

Kim and Fthenakis (2012) reviewed 22 LCA studies on nanotechnology systems, focusing on energy consumption and greenhouse gas emissions. They found that, considering a cradle-to-gate boundary, nanomaterials have a higher impact than their conventional technological options. This result is in agreement with Grubb and Bakshi (2011), who compared the impacts of the production of titanium dioxide nanoparticles for building applications with those of traditional building materials and found that nanomaterials have higher negative effect on energy consumption and material losses. Conversely, referring to the specific case of automotive exterior body panels with nano-based additives, Dinghra et al. (2010) recommend the adoption of a full life cycle perspective in order to avoid excessive emphasis on the environmental benefits of these new technologies, often associated to the use stage. In fact, the perceived environmental benefits of nano-based products in one specific stage may be overestimated if the impacts in the other life-cycle phases are not considered.

In this context, key limitations in the application of LCA to ENMs have been identified. A main critical issue is that commonly used impact assessment methods do not allow LCA to fully consider the contribution of ENMs to toxicity related impact categories (Hischier and Walser 2012; Miseljic and Olsen 2014; Gallagher et al. 2017).

Such limitation regards, at first, the scarce availability of information on the release and fate of ENMs throughout their life cycle and consequently on the potential impacts on the environment and on human health (Hischier and Walser 2012).

Moreover, the environmental impact assessment methods currently used in LCA do not fully represent the impacts of nanomaterials. In fact, the nano-specific fate, transport, and toxicity effects in the environmental compartments (air, water, and soil), which depend on typical features of nanoparticles such as the particle number, size distribution, surface charge, and surface composition, are not adequately known and modelled in the currently used methods (e.g., USEtoxTM method) (Gavankar 2012; Hischier 2014; Miseljic and Olsen 2014).

These limitations imply that LCA is currently unable to fully consider the nano-specific effects in environmental impact categories, such as human toxicity and ecotoxicity (Hischier 2014).

Some attempts have been made to develop characterization factors that consider the contribution of specific nano-products. However, these are focused on very specific applications and not generalizable. For instance, Walser et al. (2011) modelled the environmental impacts of silver nanoparticles released from T-shirts, based on literature data, while Eckelman et al. (2012) and Salieri et al. (2015) calculated, with the USEtox model, the characterization factors for the ecotoxicity of carbon nanotubes and titanium dioxide nanoparticles in freshwater, respectively.

Several reports also proposed the integration of LCA with other methods, such as multi-criteria decision analysis (MCDA) (Seager et al. 2008), risk assessment (Gavankar 2012; Grieger et al. 2012; Barberio et al. 2014) or an environmental, health and safety screening in order to take into account the toxicity information lacking in LCA (Tan et al. 2018).

In the context of application of ENMs for environmental remediation, we recently proposed an original approach to overcome the toxicology and legislative issues related to the use of nanotechnology (Corsi et al. 2018). It consists into the use of nanomaterials not directly as single units, but after they have been assembled to construct macro-dimensioned materials with an internal

nano-structure. The resulting materials should exhibit an enhanced nanoporosity, and consequently a high surface area typical of ENMs, but also a high stability, so that their fate and transport in the environment can be easily defined and managed.

While the application of LCA to nanomaterials and, more generally, the assessment of their safety and environmental risks, have been widely debated in the literature, nanoporous materials have been little investigated.

The first aim of the present study was thus to bridge this gap, focusing on the production of cellulose nanosponges (CNSs) as case study.

CNSs are adsorbent systems successfully applied for water decontamination from both organic (including emerging contaminants) and inorganic (Cd^{2+} , Zn^{2+} , Pb^{2+} , Cr^{3+} , Cu^{2+}) pollutants (Melone et al. 2015), but they have not been explored yet in terms of LCA, in order to assess their environmental performances.

These materials are synthesized following a multi-step approach: i) partial oxidation of the alcoholic groups in the C6 position of the cellulose glucopyranosic units to the corresponding carboxylic moieties; ii) de-fibrillation of the hierarchical structure of cellulose to obtain the corresponding cellulose nanofibers (CNF); iii) mixing CNF hydrogels with branched polyethyleneimine 25 kDa (b-PEI, a polymer with primary, secondary and tertiary amino groups); iv) thermal treatment in order to both introduce micro-porosity and favor cross-linking via the formation of amide bonds between CNF carboxylic units and b-PEI primary amines, thus also introducing nano-porosity in the xerogel; v) purification of CNS by washing with a methanol solvent.

There are three key reasons for the increased interest in CNSs. They can be produced from sustainable and renewable sources including agricultural waste. Moreover, they provide both micro- and nanoporosity, which enhances the amount of contaminant removed per gram of adsorbent (in the case of heavy metal ions over 200 mg/g). Furthermore, the eco-safety of the material, which was proved within a parallel research, confirms the validity of the nano-structured solution as an

alternative with respect to nano-sized systems (Corsi et al. 2018). Finally, while most of the adsorbent systems represent waste to be disposed of at the end of life, CNFs can be easily regenerated and recycled several times, while the final disposal could simply consist in the combustion of the bio-organic product.

Besides offering, to the best of our knowledge, a unique example of the application of LCA to the production of nanoporous materials, another original contribution of this study is the application of LCA from the early lab-scale stage of the device development. In fact, this approach enabled us to assess the feasibility of an environmentally-oriented production of new materials by identifying eco-design recommendations for the scale-up phase i.e. the design or the production of a material by taking into account the potential environmental impacts since the early laboratory stage. We also present a simulated scale-up model, in order to evaluate the global environmental impacts as a consequence of the optimization of the energy consuming steps.

<heading level 1> Method and case study profile

Life cycle assessment was applied to the production of innovative nanostructured materials (cellulose nanosponges-CNS) for use in soil and water remediation.

The system boundaries were established from cradle to gate, namely from the acquisition of raw materials to the production of CNS. The functional unit considered was “1 kg of CNS produced”. The impact assessment method applied in this study was the ILCD 2011 Midpoint +, which is recommended by the European Commission in the product environmental footprint methodology (European Commission, 2013). We considered the following 16 impact categories: climate change (kg CO₂ eq.), ozone depletion (kg CFC-11 eq.), human toxicity - cancer effects (CTUh), human toxicity - non-cancer effects (CTUh), particulate matter (kg PM_{2.5} eq.), ionizing radiation - human health HH (kBq U235 eq.), ionizing radiation - ecosystem E (interim) (CTUe), photochemical ozone formation (kg NMVOC eq.), acidification (molc H⁺ eq.), terrestrial eutrophication (molc N eq.), freshwater eutrophication (kg P eq.), marine eutrophication (kg N eq.), freshwater ecotoxicity (CTUe), land use (kg C deficit), water resource depletion (m³ water eq.), and mineral, fossil and

renewable resource depletion (kg Sb eq.). SimaPro 8.3 with the Ecoinvent 3.1 database for secondary data regarding the production of chemicals, and the provision of energy, water etc. was used for the analysis.

The study covered three production systems (PS), from the laboratory scale to a modelled scale-up system, to guide the eco-design of the PS and assess the improvements achieved.

An initial analysis (PS_lab) was carried out at the laboratory scale to identify the main environmental hotspots, namely processes and stages that provide the largest contribution to the global environmental impacts. Focusing on these, we suggested improvements actions, already at the lab-scale, such as the change in washing solvent and temperature. PS_lab-optimized analysis was carried out on the optimized process, to assess the environmental impact reduction achieved. Since another relevant area contributing to the global environmental impacts was related to the energy consuming processes, which could not be improved at the lab-scale, we therefore modelled a simplified scaled-up production process, where the energy consuming steps could be effectively optimized. PS_scale-up analysis confirmed the environmental benefits achieved.

The production system of CNS consists in three steps:

1. Cellulose oxidation
2. CNF production by sonication
3. CNS synthesis by CNF crosslinking in the presence of b-PEI.

The substrate used for this process was cellulose from recycled pulp.

In step 1, bulk cellulose is chemically oxidized by 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)/NaClO/KBr, following the original protocol reported by Isogai and et al. (2011). The TEMPO-oxidized cellulose is then acidified with chloridric acid (HCl) to facilitate precipitation and is then recovered by filtration and washed with water.

In step 2, TEMPO-oxidized cellulose is dispersed in a sodium hydroxide (NaOH) aqueous solution, and the mixture undergoes sonication until a homogeneous hydrogel is obtained, indicating the

formation of CNF. The nano-dimensioned fibres are filtered after HCl acidification and washed with deionized water.

In step 3, CNFs are dispersed in water and mixed with b-PEI. The concentration of CNFs in the final mixture should range between 2.5 and 3.5% w/v (weight of CNF/volume of solvent). The viscous gel obtained is then sonicated, transferred in an appropriate mold, frozen and freeze-dried. The resulting xerogel undergoes thermal treatment in order to promote the cross-linking between CNF and b-PEI. Finally, non-reticulated components are washed away using a methanol solvent, thereby producing a sponge-like material. Figure 1 summarizes the three steps.

FIGURE 1 ABOUT HERE

Data regarding the CNS synthetic protocol were collected following the procedures previously reported (Melone et al. 2015; Fiorati et al. 2017). In the lab-scale production, the energy consumption of the electric appliances (e.g., stirrer, freeze-dryer, oven) was estimated from the power of the appliances per time used, taking into account that this approach might overestimate the energy consumption per unit produced. In addition, other aspects were not optimized, such as solvent and catalyst recycling and refrigerant water recycling, which are usually not done in a research laboratory. Table 1 reports the main life cycle inventory data regarding the original lab-scale protocol referring to 100 grams of starting material.

TABLE 1 ABOUT HERE

The environmental hotspots revealed by PS_lab analysis mainly regarded step 3 (CNS synthesis) and led to the following two modifications to the original protocol, which were then implemented at the lab-scale:

- replacing methanol in the washing step with water (12.5 L), which is considerably safer and cheaper
- decreasing the solvent heating temperature during the final washing steps, which reduces the energy consumption, but also saves 720 L of water used as cooler during step 3.

As the purification step is intended to remove un-reticulated b-PEI, we experimentally verified that the use of water in the washing procedure was even more efficient and did not affect the final morphology and performance of the nanostructured material. In fact, switching to water also significantly decreased the solvent heating temperature up to almost room temperature, thus increasing the purification efficiency.

In order to optimize the energy-consuming processes, which emerged as major contributors to the environmental impacts as evidenced by PS_lab, we developed a scale-up model adapting the equations indicated by Piccinno et al. (2016). This framework is a simplified way of providing useful data for an initial LCA assessment of the potential impacts of a material in a future industrial scale. The scale-up model was based on the reaction steps and the quantities of substrates defined in the laboratory protocol. A simple plant flow diagram including all the steps was then designed (Figure 2). Each step, modelled as a batch process, was scaled up according to the equations presented by Piccinno et al. Finally, the single steps were linked to each other and heat and material (e.g., solvents) recovery was generally included.

Piccinno's approach entails the linear scale-up of each reactant, since laboratory procedures involve stoichiometric quantities. The amount of solvent is also scaled up linearly to maintain the reagents concentration. On the other hand, the energy consumption for each process step is calculated by either adopting average energy consumption values from the literature or applying simplified equations that have a non-linear scale-up. The equations enable the calculation of energy consumption of each step, using parameters obtained from the literature and specific values from our system (e.g., density of the mixture, mass of the reactants, heat capacity). Since Piccinno's framework does not provide indication on how to scale-up the freeze-drying step, we started from the technical specification of an

industrial freeze-dryer, namely from the capacity of the condenser, which enabled us to calculate the quantity of the input reagents and the size of all the process steps. On the basis of a FD1500 freeze dryer model from Cuddon (<https://www.cuddonfreezedry.com/>), we estimated, through a material balance, that each production batch starts with 62 kg of cellulose and reacts in 1290 L volume vessels. The appropriate parameters were thus calculated to feed the equations. This enabled us to calculate the energy consumption of each reactive step (batch stirring, homogenising, filtering, pre-freezing, heating, washing and drying, etc.). In the inter-process steps, we included the recycling of the solvent used for washing (water). In this preliminary model, we did not include energy recovery, which would certainly further contribute to the process.

This engineering-based approach did not entail collecting empirical data (as it is expected to be used when data are not yet available), therefore uncertainties could not be defined directly.

FIGURE 2 ABOUT HERE

Table 2 reports the life cycle inventory data obtained from the model, which were used in the PS_scale-up LCA analysis.

TABLE 2 ABOUT HERE

<heading level 1> Results

<heading level 2> Life cycle impact assessment of the lab scale production of CNS (PS_lab)

The PS_lab analysis refers to the original lab-scale production protocol. Table 3 reports the results for all the impact categories, with the contributions of the three main steps and the focus on the most significant, those of step 3.

TABLE 3 ABOUT HERE

This stage contributed to water resource depletion by about 80% with 53 m³ water eq., 90% with 2964 kg CO₂ eq. to climate change and 95% with 16.8 molcH⁺ eq. to acidification.

The energy-consuming processes of step 3 were also the most dominant, followed by water consumption, solvent disposal and input materials.

Freeze-drying and heating contributed the most (Fig. 3). For instance, focusing on the climate change impact category, the contribution of freeze drying was 45% with 1.34 kg CO₂ eq., while thermal treatment accounted for 37% (1.10 kg CO₂ eq.). The heating of the solvent in the final washing step was 8% of the impact (232 kg CO₂ eq.). Similar contributions were found for other impact categories such as ozone depletion, particulate matter, ionizing radiation, photochemical ozone depletion, acidification, eutrophication, and land use

Water consumption for the cooling system during the final washing contributed to water resource depletion by about 70% (37.8 m³ water eq.), and 60% to mineral and fossil and renewable resource depletion (8.61E-03 kg Sb eq.). Finally, methanol used as washing solvent accounted for about 7% of the mineral and fossil and renewable resource depletion, with 1.03E-03 kg Sb eq.

FIGURE 3 ABOUT HERE

*<heading level 2> Life cycle impact assessment of the optimized lab scale production of CNS
(PS_lab-optimized)*

The results of PS_lab-optimized analysis revealed the benefits of the optimization of the washing step, showing a decrease in the potential environmental impacts, with respect to the PS_lab results, although within the same order of magnitude (Table 4).

TABLE 4 ABOUT HERE

In a first purification protocol finalized to the removal of un-reacted b-PEI, methanol was chosen as washing solvent, by operating at 60 °C. This procedure was followed at laboratory scale in order to fasten this step and to facilitate b-PEI removal. However, PS_lab results showed the potential impact of this choice on the overall CNS production. For this reason, we envisioned that, being b-PEI highly water soluble, water could be considered as an alternative solvent for this purpose. Moreover, we also envisioned that, while operating at 60 °C could favour b-PEI solubilization, making purification more efficient, on the other side such a relatively high temperature could promote hydrolysis of amide bonds, inducing partial degradation of original CNS. As a consequence, methanol was replaced with water as a washing solvent and the temperature of the solvent was decreased from 60°C to 30°C. This modification resulted in a global modest decrease in the environmental impacts of the total LCA results for the CNS production process, ranging between 2 and 14% depending on the categories considered. However, focusing on step 3 (CNS production), the elimination of methanol as washing solvent significantly reduced the impact of the materials. For instance, it reduced their impact on climate change by 88% from 38 kg CO₂ eq. to 4.3 kg CO₂ eq. At the same time, the lowering of washing temperature (from 60°C to 30°C) reduced the impact of the energy consuming processes on climate change by about 11%, from 2,759 kg CO₂ eq. to 2,461 kg CO₂ eq. Moreover, replacing methanol with water also reduced the impacts on climate change in the solvent disposal stage by almost 100%, moving from 81.9 kg CO₂ eq. to 0.09 kg CO₂ eq.

<heading level 2> Life cycle impact assessment of the scale-up production of CNS (PS_scale-up)

The PS_scale-up results are reported in Table 5, with the contribution of each main step and a focus on step 3.

TABLE 5 ABOUT HERE

These results highlighted a reduction in the environmental impacts by about two orders of magnitude with respect to PS_lab and PS_lab-optimized analyses, for all the impact categories. As examples, climate change impact category decreased from 3,343 kg CO₂ eq. in PS_lab and 2,930 kg CO₂ eq. in PS_lab-optimized to 27.4 kg CO₂ eq. in PS_scale-up. Particulate matter impact category decreased from 1.18 kg PM_{2.5} in PS_lab and 1.04 kg PM_{2.5} in PS_lab -optimized to 1.77E-02 kg PM_{2.5} in PS_scale-up. For photochemical ozone depletion impact category, there was a decrease from 7.9 kg NMVOC eq. in PS_lab and 6.96 kg NMVOC eq. in PS_lab-optimized to 7.49E-02 kg NMVOC eq. in PS_scale-up. For acidification impact category, we found a reduction from 17.3 molc H⁺ eq. in PS_lab and 15.2 molc H⁺ eq. in PS_lab-optimized to 0.17 molc H⁺ eq. in PS_scale-up .

In PS_scale-up, step 3 (CNS production) confirmed the largest impact, followed by step 1 (cellulose oxidation). With regard to climate change, the CNS production stage contributed with 20.36 kg CO₂ eq., while cellulose oxidation contributed with 6.7 kg CO₂ eq.

The energy-consuming processes in step 3 impacted by about 60% on several categories, such as climate change (17.2 kg CO₂ eq.), photochemical ozone formation (0.045 kg NMVOC eq.), acidification (0.098 molcH⁺ eq.), terrestrial eutrophication (0.151 molc N eq.), and land use (18.5 kg C deficit). Among the energy consuming processes, freeze drying still had the most impact in several categories, with about 16 kg CO₂ eq. for climate change, 4.12E-02 kg NMVOC eq. for photochemical ozone formation, 9.1E-02 molc H⁺ eq. for acidification, 0.14 molc N eq. for terrestrial eutrophication, and 17.1 kg C deficit for land use.

Materials were the main contributors to other impact categories such as ozone depletion (70%, with 1.51 E-06 kg CFC-11 eq.), human toxicity (70% with 3.84E-07 CTUh), freshwater eutrophication and freshwater ecotoxicity (65% with 5.32E-04 kg P eq. and 3.72 CTUe, respectively), and mineral and fossil and renewable resource depletion (95% with 2.78E-05 kg Sb eq.).

Among the materials, the cross-linker had the largest contribution with 5.85E-05 kg CFC-11 eq. for ozone depletion, 3.55E-07 and 3.98E-08 CTUh for human toxicity, non-cancer and cancer,

respectively, 1.35E-04 kg P eq. for freshwater eutrophication, 2.79 CTUe for freshwater ecotoxicity and 1.67E-04 kg Sb eq. for mineral and fossil and renewable resource depletion.

Water consumption contributed by about 10% to water resource depletion category and, finally, the treatment needed for the internal recycling of the solvent contributed by less than 10% to some of the impact categories (e.g., human toxicity, eutrophication and water resource depletion) (Figure 4).

FIGURE 4 ABOUT HERE

<heading level 1> Discussion

The results of the present study are in agreement with indications already emerged from the literature, regarding the importance of going to a scale-up level in order to provide a sound assessment of the environmental impacts of the production process of a new material (Hetherington, 2014). LCA confirmed to be very useful, at this early research stage, for identifying those phases which have the most impact on the environment, favouring an optimal eco-design of the process (Frischknecht 2009).

In this study, the environmental impact results calculated with PS_lab analysis were two orders of magnitude higher than those of other materials produced at the industrial level and used for similar applications (i.e., water and soil remediation). For instance, while the carbon footprint of our lab-produced CNS was about 3,400 kg CO₂ eq./kg, carbon black is 1.82 kg CO₂eq./kg (Ecoinvent 3.1). Therefore, this confirmed the need to scale-up the process in order to obtain useful results for a comparison with other similar materials already produced at the industrial scale.

On the other hand, the contribution analysis of the impacts showed that, in the lab-scale CNS production, the largest contribution stemmed from step 3 (CNS synthesis). In particular, freeze drying and heating steps had the largest impacts contribution. Other relevant contributions stemmed from the materials (chemicals and solvents) used in the process, namely b-PEI cross-linker and, above all, methanol used in the final washing step of the CNS product. The use of methanol also

negatively affected the solvent disposal stage, as it was treated as a hazardous waste. These outcomes drove some optimizations that could be already implemented at the lab scale, regarding the washing procedure. Although the impacts assessed with PS_lab-optimized analysis were still of the same order of magnitude as the results of PS_lab, they confirmed their positive effects.

The following PS_scale-up analysis highlighted that a simplified scale-up model as that proposed in this work could provide a reduction of the environmental impacts by about two orders of magnitude in all the impact categories with respect to the laboratory synthesis. The scale-up followed an engineered-based theoretical approach, which did not include empirical data that might be useful for validating the model and for calculating the level of uncertainty. Therefore, at this stage, this evaluation should be considered as a preliminary estimation of the actual environmental impacts of the scale-up. Step 3 in the scale-up process still had the largest contribution. However, the results showed not only a decrease in the total impacts but also that the relative contribution of the most important energy consuming steps in this step, namely lyophilisation and thermal heating, were reduced from about 90% of the lab scale to about 60% of the scale-up scenario for most of the impact categories. Both lyophilisation and heating were crucial in the synthetic protocol and therefore could not be replaced. In fact, freezing leads to the formation of water crystals, which guarantee random micro-distances among fibres. The subsequent lyophilisation promotes the formation of the xerogel, where water crystals give way to micropores, preventing the collapse of the structure. Finally, heating promotes the condensation between amino groups of b-PEI and carboxylic moieties of CNF. We therefore recommend a further accurate modelling of the scale-up, in particular for the lyophilisation step. As regards to the other improvements made in the scale-up, the internal recycling of the water used for the washing process in step 3 helped to decrease the impacts on water depletion impact category from 52.1 m³ water eq. at the lab scale to 0.137 m³ water eq. We expect further improvements in the environmental impacts in the scale-up process if energy recovery solutions are included in the reaction connection steps.

In terms of the specific nanostructured materials based on cellulose, using nanostructured materials rather than nanosized solutions overcomes issues related to eco- and health-safety. The synthetic strategy herein reported has two main advantages compared to standard adsorbent approaches (Corsi et al. 2018): i) the production of fibres under mild conditions, according to a standard oxidation protocol (Pierre et al. 2017); ii) the promotion of efficient cross-linking by thermal treatment.

<heading level 1> Conclusions

LCA was used as an eco-design tool to guide the optimization and the scale-up of the synthesis of an innovative nanostructured material based on cellulose (CNS), to be used for nanoremediation. At the lab-scale, the energy consuming processes and the final washing step procedures were found to contribute the most to the environmental impacts. The washing procedure could be already optimized at the lab scale by replacing methanol with water as a solvent and lowering heating temperature of the solvent itself. Benefits achieved could be assessed with a second PS_lab-optimized analysis, although within the same order of magnitude of the original lab scale analysis.

To optimize the energy- consuming processes, which had the largest contribution to the environmental impacts, we developed a simplified scale-up model of the CNS production. LCA revealed that this led to a reduction in the global environmental impacts by about two orders of magnitude with respect to the laboratory scale synthesis.

Therefore, our analysis provided an example of how LCA can be a useful tool in the early research stage to indicate the most suitable eco-design actions to reduce the environmental impacts in the production process of innovative materials.

Although we achieved a significant improvement with our scale-up model, we are aware that the development of real pilot and pre industrial scales would provide further improvements in the modelling, with the necessary data to correctly assess the environmental impacts of the CNS

production. For instance, LCA showed that, even at this scale, freeze-drying and thermal heating, which are key steps in ensuring the final characteristics of the material, have the most negative impact on the environment. Therefore, their scale-up modelling and implementation should be carefully considered. We are aware that, due to these energy intensive steps, the production of CNS might be less competitive than other similar materials, (e.g., carbon black) from an environmental impact point of view. However, the final use and the end-of-life stages should be also included in the LCA assessment, thereby extending the system boundaries from cradle to grave. In particular, the use stage (e.g., in water/soil remediation) should take into consideration the improved performance due to the nanostructure of the CNS, which results in a higher decontamination efficiency per gram of sorbent used. Finally, while most of the adsorbent systems represent waste to be disposed of at the end of life, CNS can be regenerated and recycled several times, and the final disposal would simply consist in the combustion of the bio-organic product. In this context, the ongoing experimental work on CNS will provide further data for the completion of the LCA analysis.

Our study also highlights some policy implications. An example regards the importance of using LCAs for new technologies. Policy makers are responsible for encouraging the diffusion of emerging technologies to favour new solutions of society practical problems. These policies encourage economic growth, but also raise new questions regarding health, safety and environmental risks. By applying LCA since the early stage of development, researchers could suggest the adoption of eco-designed solutions, which could lead to the reduction of the key environmental impacts, as shown by our results and as already partially observed by other studies (Daddi et al. 2017; Bartolozzi et al. 2018). Research on new materials and technologies associated with increasingly sophisticated tools are needed in order to assess the safety and environmental implications.

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Table 1. Life cycle inventory of lab scale synthesis of CNS¹

STEP 1: cellulose oxidation		
Input	Quantity	Unit
Potassium bromide (KBr)	15.4	g
TEMPO	2.15	g
H ₂ O (reaction solvent)	6.0	L
Cellulose from recycled pulp	100	g
NaClO	47.5	g
NaOH	24	g
HCl	28.5	g
H ₂ O (washing step)	6	L
Output		
Oxidized cellulose	73	g
Energy consumptions		
Electricity (stirring)	18	Wh
Water (vacuum pump)	151	L
Wastes		
Water	12	L
Filter (paper)	1	unit
STEP 2: CNF production		
Input	Quantity	Unit
Oxidized cellulose (output STEP 1)	73	g
NaOH	10	g
Water (reaction)	2.25	L
Water (washing)	12.5	L
HCl	5.77	g
Ice (cooling)	1	kg
Water (cooling)	5	L
Output		
Cellulose nanofibers (CNF)	73	g
Energy consumptions		
Electricity (sonication and stirring)	11.3	Wh
Water (vacuum pump)	150	L
Wastes		
Water	14.75	L
Filter (paper)	1	unit
STEP 3: CNS production		
Input	Quantity	Unit
CNF	73	g
bPEI (25 KDa)	146	g
Water (reaction)	1.75	L
Ice (cooling)	1	kg
Water (cooling)	5	L
Methanol	7.15	kg
Output		
Cellulose nanosponge (CNS)	156	g
Energy consumptions		

Electricity (stirring)	5	Wh
Electricity (sonication)	10.5	Wh
Electricity (Freezing)	427	Wh
Electricity (Freeze-drying)	8	kWh
Electricity (thermal treatment)	6	kWh
Electricity (washing step heating)	1.25	kWh
Electricity (drying)	6	kWh
Water (cooling)	720	L
Wastes		
Methanol	7.15	kg

Note: ¹Melone et al. 2015; Fiorati et al. 2017

Table 1. Life cycle inventory of scale-up synthesis of CNS

STEP 1: cellulose oxidation		
Input - materials	Quantity	Unit
Cellulose from recycled pulp	61.88	kg
Potassium bromide (KBr)	9.53	kg
TEMPO	1.33	kg
Deionized water	1.33	m ³
Sodium ipochlorite (NaClO)	269	kg
Sodium hydroxide (NaOH)	371	kg
Chloridric acid (HCl)	210.22	kg
Input - water		
Cooling water (internal recycling)	3,713	kg
Input - energy		
Electricity - stirring (step 1)	39	Wh
Electricity - pumping	23.6	Wh
Output		
Oxidized cellulose	46.4	kg
STEP 2: CNF production		
Input - materials	Quantity	Unit
Oxidized cellulose (from Step 1)	46.40	kg
Sodium hydroxide (NaOH)	6.35	kg
Input - water		
Cooling water (internal recycling)	7,946	kg
Input - energy		
Electricity - Homogenizing (step 2)	25.4	kWh
Electricity - stirring (step 3)	39.0	Wh
Electricity - filtration (step 4)	7.1	kWh
Electricity - pumping	23.6	Wh
Output		
Cellulose nanofibers (CNF)	46.4	kg
STEP 3: CNS Production		
Input - materials	Quantity	Unit
Cellulose nanofibers (CNF)	46.4	kg
Deionized water	1,500	l
bPEI	46.4	kg
Citric acid	17.16	kg
Input - energy		
Electricity - stirring (step 5)	39	Wh
Electricity -Pre-freeze drying (step 6)	225.3	kWh

Electricity --freeze drying (step 7)	3,000	kWh
Electricity -heating (step 8)	5.5	kWh
Electricity –washing and drying (step 9)	0.22	kWh
Electricity -grinding (step 10)	15.48	kWh
Electricity -pumping	23.6	Wh
Output		
Cellulose nanosponges (CNS)	110	kg

Table 3. PS_lab results for the lab-scale production of CNS per 1 kg CNS produced

Impact category	Unit	Total	Recycled Cellulose pulp	Cellulose oxidation	CNF production	CNS production	Energy - CNS production	Materials - CNS production	Water- CNS production	Waste solvent disposal - CNS production
Climate change	kg CO ₂ eq	3,343.13	2.14	172.89	203.88	2964.21	2759.34	38.69	86.36	81.88
Ozone depletion	kg CFC-11 eq	2.78E-04	1.95E-07	6.61E-06	7.63E-06	2.64E-04	2.43E-04	9.92E-06	8.44E-06	2.36E-06
Human toxicity, non-cancer effects	CTU h	1.20E-04	3.88E-07	9.75E-06	1.01E-05	1.00E-04	6.18E-05	2.87E-06	3.43E-05	1.24E-06
Human toxicity, cancer effects	CTU h	2.44E-05	4.13E-08	2.05E-06	2.10E-06	2.02E-05	1.13E-05	2.93E-07	8.49E-06	1.27E-07
Particulate matter	kg PM _{2.5} eq	1.18	2.30E-03	3.62E-02	4.14E-02	1.10E+00	1.01E+00	2.64E-02	5.23E-02	1.26E-02
Ionizing radiation HH	kBq U235 eq	202.54	0.09	3.18	3.52	195.75	185.14	0.98	9.11	0.52
Ionizing radiation E (interim)	CTU e	1.75E-03	6.73E-07	2.50E-05	2.78E-05	1.70E-03	1.61E-03	7.65E-06	7.19E-05	3.93E-06
Photochemical ozone formation	kg NM VOC eq	7.90	0.01	0.14	0.16	7.59	7.17	0.14	0.25	0.04
Acidification	molc H ⁺ eq	17.29	0.03	0.23	0.26	16.77	15.83	0.38	0.50	0.05
Terrestrial eutrophication	molc N eq	26.74	0.09	0.50	0.58	25.57	24.30	0.32	0.79	0.16
Freshwater eutrophication	kg P eq	1.04E-01	3.96E-04	3.47E-03	3.85E-03	9.58E-02	8.55E-02	2.29E-03	6.99E-03	9.85E-04
Marine eutrophication	kg N eq	2.46	8.32E-03	4.64E-02	5.25E-02	2.35	2.22	3.89E-02	7.05E-02	1.45E-02
Freshwater ecotoxicity	CTU e	858.91	23.53	37.81	40.65	756.92	598.54	40.37	111.00	7.02
Land use	kg C deficit	3,487.83	55.56	65.82	75.73	3290.73	3069.53	85.82	115.42	19.96
Water	m ³	70.31	0.82	7.99	8.03	53.46	15.95	-0.48	37.99	2.21E-03

Impact category	Unit	Total	Recycled Cellulose pulp	Cellulose oxidation	CNF production	CNS production	<i>Energy - CNS production</i>	<i>Materials - CNS production</i>	<i>Water- CNS production</i>	<i>Waste solvent disposal - CNS production</i>
resource depletion	wate r eq									
Mineral. fossil & ren resource depletion	kg Sb eq	1.92E- 02	9.10E- 05	2.23E- 03	2.29E- 03	1.46E-02	4.47E-03	1.37E- 03	8.56E- 03	2.15E-04

Table 4. PS_lab-optimized results for the optimized lab scale production referred to 1 kg CNS produced.

Impact category	Unit	Total	Recycled Cellulose Pulp	Cellulose oxidation	CNF production	CNS production	CNS production Water	CNS production energy	CNS production -raw materials
Climate change	kg CO ₂ eq	2.93E+03	2.14E+00	1.75E+02	2.03E+02	2.55E+03	8.53E+01	2.46E+03	4.31E+00
Ozone depletion	kg CFC-11 eq	2.41E-04	1.95E-07	6.79E-06	7.55E-06	2.26E-04	8.44E-06	2.17E-04	1.32E-06
Human toxicity, non-cancer effects	CTUh	1.12E-04	3.88E-07	1.07E-05	1.01E-05	9.06E-05	3.43E-05	5.51E-05	5.40E-07
Human toxicity, cancer effects	CTUh	2.28E-05	4.13E-08	2.09E-06	2.09E-06	1.86E-05	8.49E-06	1.00E-05	5.77E-08
Particulate matter	kg PM2.5 eq	1.04E+00	2.30E-03	3.72E-02	4.10E-02	9.56E-01	5.23E-02	8.99E-01	4.37E-03
Ionizing radiation HH	kBq U235 eq	1.82E+02	8.57E-02	3.62E+00	3.45E+00	1.75E+02	9.11E+00	1.65E+02	2.16E-01
Ionizing radiation (interim) E	CTUe	1.57E-03	6..73E-07	2.90E-05	2..72E-05	1..51E-03	7..19E-05	1..44E-03	1..72E-06
Photochemical ozone formation	kg NMVOC eq	6.96E+00	8.36E-03	1.43E-01	1.55E-01	6.66E+00	2.50E-01	6.39E+00	1.19E-02
Acidification	molc H ⁺ eq	1.52E+01	2.69E-02	2.41E-01	2.58E-01	1.47E+01	4.99E-01	1.41E+01	3.00E-02
Terrestrial eutrophication	molc N eq	2.37E+01	9.35E-02	5.19E-01	5.69E-01	2.25E+01	7.91E-01	2.17E+01	5.12E-02
Freshwater eutrophication	kg P eq	9.18E-02	3.96E-04	3.74E-03	3.82E-03	8.38E-02	6.99E-03	7.63E-02	3.30E-04
Marine eutrophication	kg N eq	2.18E+00	8.32E-03	4.83E-02	5.17E-02	2.07E+00	7.05E-02	1.99E+00	1.03E-02
Freshwater ecotoxicity	CTUe	7.53E+02	2.35E+01	3.90E+01	4.04E+01	6.50E+02	1.11E+02	5.34E+02	4.04E+00
Land use	kg C deficit	3.06E+03	5.56E+01	6.86E+01	7.46E+01	2.86E+03	1.15E+02	2.74E+03	7.47E+00
Water resource depletion	m3 water eq	6.91E+01	8.23E-01	8.02E+00	8.03E+00	5.23E+01	3.80E+01	1.42E+01	7.82E-02
Mineral, fossil & ren resource depletion	kg Sb eq	1.76E-02	9.10E-05	2.28E-03	2.29E-03	1.29E-02	8.56E-03	3.99E-03	3.27E-04

Table 5. PS_scale-up results for the modelled scale up production of CNS per 1 kg CNS produced

Impact category	Unit	Total	Recycled Cellulose Pulp	Cellulose oxidation	CNF production	CNS production	CNS production-Water	CNS production-Materials	CNS production-Energy
Climate change	kg CO ₂ eq	2.74E+01	2.50E-01	6.68E+00	1.50E-01	2.04E+01	2.32E-02	3.21E+00	1.72E+01
Ozone depletion	kg CFC-11 eq	5.43E-06	2.86E-08	2.72E-06	5.70E-08	2.62E-06	6.25E-09	1.11E-06	1.51E-06
Human toxicity, non-cancer effects	CTUh	2.87E-06	5.45E-08	1.77E-06	2.15E-07	8.27E-07	3.60E-09	4.40E-07	3.84E-07
Human toxicity, cancer effects	CTUh	2.19E-07	4.74E-09	9.42E-08	6.29E-09	1.13E-07	6.86E-10	4.29E-08	7.00E-08
Particulate matter	kg PM2.5 eq	1.77E-02	2.19E-03	5.47E-03	1.08E-04	9.94E-03	2.09E-05	3.67E-03	6.27E-03
Ionizing radiation HH	kBq U235 eq	2.10E+00	2.00E-02	7.40E-01	1.00E-02	1.33E+00	1.30E-03	1.78E-01	1.15E+00
Ionizing radiation E (interim)	CTUe	1.81E-05	1.54E-07	6.42E-06	7.14E-08	1.14E-05	1.07E-08	1.41E-06	1.00E-05
Photochemical ozone formation	kg NMVO C eq	7.49E-02	1.42E-03	1.85E-02	4.19E-04	5.45E-02	5.52E-05	9.99E-03	4.46E-02
Acidification	mole H ⁺ eq	1.68E-01	2.55E-03	4.08E-02	1.00E-03	1.24E-01	1.23E-04	2.54E-02	9.85E-02
Terrestrial eutrophication	mole N eq	2.69E-01	5.33E-03	6.72E-02	2.06E-03	1.95E-01	1.91E-04	4.36E-02	1.51E-01
Freshwater eutrophication	kg P eq	1.60E-03	2.94E-05	6.84E-04	7.47E-05	8.10E-04	1.50E-06	2.78E-04	5.32E-04
Marine eutrophication	kg N eq	3.28E-02	6.01E-04	7.70E-03	1.60E-03	2.29E-02	1.71E-05	9.05E-03	1.38E-02
Freshwater ecotoxicity	CTUe	1.10E+01	1.90E-01	3.24E+00	3.70E-01	7.21E+00	1.21E-02	3.48E+00	3.72E+00
Land use	kg C deficit	3.08E+01	7.30E-01	6.44E+00	4.00E-01	2.32E+01	1.98E-02	4.65E+00	1.85E+01
Water resource depletion	m ³ water eq	1.54E-01	1.80E-03	3.14E-02	-2.18E-02	1.42E-01	2.24E-03	4.10E-02	9.92E-02
Mineral. fossil & ren resource depletion	kg Sb eq	6.19E-04	2.55E-05	2.81E-04	3.70E-06	3.09E-04	1.13E-06	2.80E-04	2.78E-05

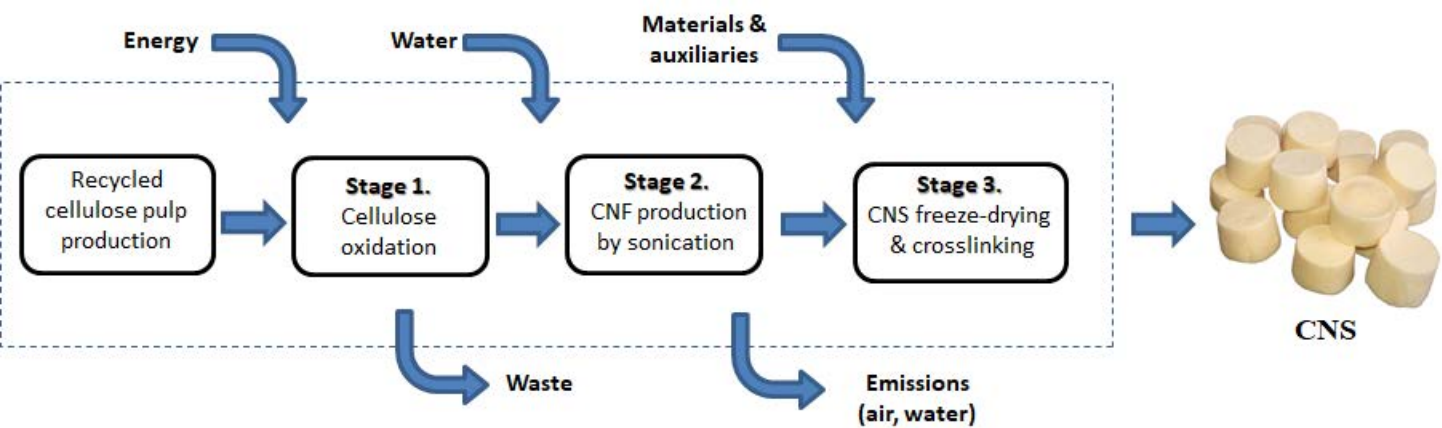


Figure.1. Simplified scheme of the synthesis of cellulose nanosponges (CNS)

1. STIRRING



2. HOMOGENIZING



3. STIRRING



4. FILTERING



5. STIRRING



6. PRE-FREEZING



7. FREEZE-DRYING



8. HEATING



9. WASHING &
DRYING



10. GRINDING

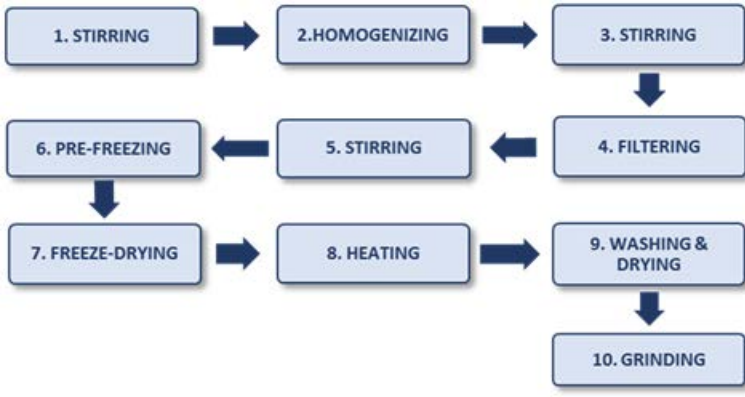


Figure 2. Flow chart of the scaled-up process.

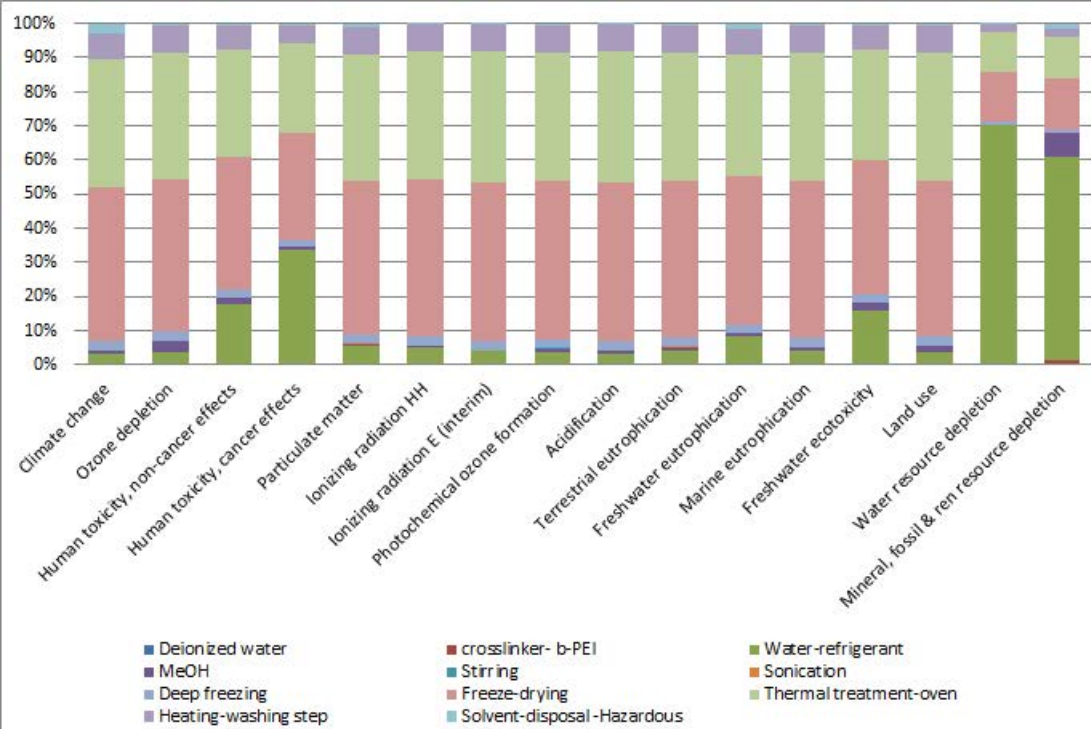


Figure 3. Contribution analysis of stage 3 of lab scale production. Underlying data used to create this figure can be found in Supporting Information

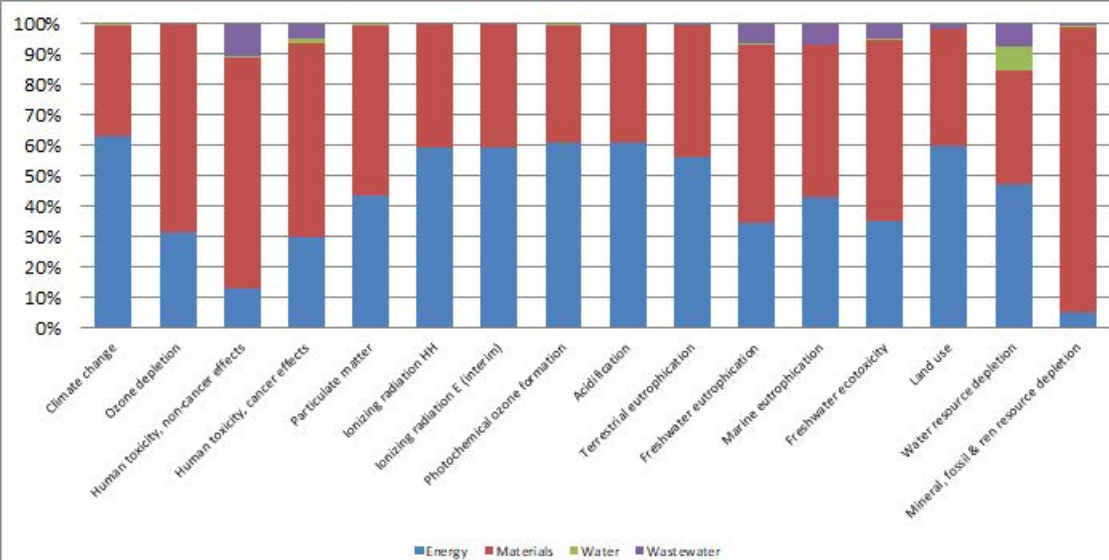


Figure 4. Detailed contribution analysis for stage 3 of scaled-up CNS production. Underlying data used to create this figure can be found in Supporting Information