LCA applied to nano scale zero valent iron synthesis

Florinda Martins[1] · **Susana Machado**[1] · **Tomás Albergaria**[1] · **Cristina Delerue-Matos**[1]

✉ Florinda Martins
ffm@isep.ipp.pt

[1] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal

Abstract

Purpose Application of zero valent iron nanoparticles is an innovative technology for ground water treatment and soil remediation. There are several methods to synthesise nano scale zero valent iron (nZVI), namely through bottom-up methods which consists on chemical reactions using strong reducing agents. In this work, the environmental impacts and costs were determined for two methods, namely the traditional one that uses sodium borohydride and the green method that uses extracts obtained from natural products.

Methods The consideration of environment and economic aspects in the earlier stages of the synthesis processes and in the development of new materials is of great importance since it can help to decide if alternative methods are promising and should be further developed aiming more sustainable processes. In this work, life cycle assessment (LCA) was used as an ecodesign strategy evaluating environmental performance of the two synthesis methods, identifying critical stages of the synthesis processes of nZVI. An economic evaluation and a sensitivity analysis considering a different scenario for electricity production were also performed.

Results and discussion The results obtained in this study showed that the green synthesis method presents lower environmental impacts than the traditional one, roughly 50% lower in the first scenario. In the second scenario, environmental impact of green synthesis corresponds to 38% of the environmental impact of traditional synthesis. In the green method, the critical stage is the extraction process which is closely related to the electricity production. In the traditional method, the reactant use is the critical stage that is related to the production of sodium borohydride. The economic evaluation indicated that the traditional synthesis method is much more expensive than the green synthesis (roughly eight times higher).

Conclusions From the results obtained, it is possible to conclude that the green synthesis method presents lower environmental impacts in both scenarios and lower costs than the traditional synthesis.

Keywords LCA · Nano zero valent iron · Soil remediation · Sustainability · Synthesis

1 Introduction

Zero valent iron has been successfully used for the removal of a wide range of pollutants such as chlorinated hydrocarbons, nitrobenzenes, chlorinated phenols, polychlorinated biphenyls (PCB) and heavy metals from soils (Dong et al. 2010; Wua et al. 2012). The recent advances of nanotechnology contributed to the development of new synthesis methods of zero valent iron nanoparticles (nZVI) (Carroll et al. 2013). This nanomaterial has several advantages over the micro-scale particles, namely the increase in the degradation reaction rate, the decrease on the reductant dosage and the generation of a non-toxic end product (Hwang et al. 2011a). The synthesis methods of nanoparticles are usually divided into two distinct approaches: top-down methods, such as vacuum sputtering, and bottom-up methods using chemical synthesis (Machado et al. 2013; Li et al. 2006). The bottom-up methods are often used for the synthesis of nZVI through the reduction of ferric or ferrous salts using strong reducing agents (Poursaberi et al. 2012; Sun et al. 2006, 2007; Hwang et al. 2011b). This process is relatively simple, since it does not require specific or expensive equipment and the obtained product presents high homogeneity (Hwang et al. 2011a). The traditional bottom-up method uses sodium borohydride as reductant which has high toxicity (New Jersey Department of Health and Senior Services 1999) raising environmental concerns due to the possible negative impacts on the environment. The fact that during the nZVI synthesis gaseous hydrogen is formed raises also safety concerns. Incorporating environmental concerns in the synthesis of new products is not new and green chemistry principles can be very helpful in achieving more sustainable products. This led to the development of new methods for the green synthesis of nZVI using extracts from natural products or wastes (Machado et al. 2013; Chrysochoou et al. 2012). The main advantages of these methods are the low toxicity of the reducing agent (the natural extracts) and the valorisation of natural products that in some cases can be considered wastes and require costs for an adequate disposal.

Life cycle assessment (LCA) is a methodology that studies and evaluates environmental impacts caused by a product or service throughout its life cycle, from extraction of raw materials to final stage when the product becomes a waste. It considers all material and energy flows in every stage of product life. LCA is performed in four phases: purpose and scope, inventory, impact assessment and interpretation, and can also be used in a gate to gate approach analysing a process in the products' life cycle. In the impact assessment phase, the potential environmental impacts associated with the use of raw materials, energy, emissions and waste are evaluated. This evaluation is calculated based on the results of inventory, which is related to the inputs and outputs, and can be performed in several steps (of which the first three are mandatory and the following are optional): Selection—selection of model and impact categories; Classification—the different substances / compounds are placed in each category; Characterisation—calculation of the value of the indicator; Normalisation—calculation of the magnitude in relation to a reference value; Aggregation—consists in joining the different categories, taking into account the type of damage; and Weighing—allocation of a certain weight to each category by the importance of each.

In the last phase of LCA, interpretation, the conclusions are generated and the possibilities to reduce environmental impacts are indicated.

LCA methodology has been applied with success to several areas adding more information for developing products, processes and helping in the decision making process (Ling-Chin et al. 2016; Rodríguez et al. 2016).

LCA applied in soil remediation is usually used to evaluate the performance of different technologies (Suer and Andersson-Sköld 2011; Morais and Delerue-Matos 2010; Cappuyns 2010; Inoue and Katayama 2011), comparing environmental impacts associated with each remediation technology. The need and demand of technology innovations led to the investment and development in nanotechnology. These advances ranged almost all scientific domains and brought an increase on process efficiencies, materials performance among other benefits. However, the development is taking different paths namely the inclusion of green principles in the nanotechnology. In this area, the green chemistry is merging with nanotechnology leading to more sustainable and efficient processes/materials.

The absence of studies and knowledge concerning the environmental impacts of the different methods of synthesis of nZVI led to this work, where LCA was used as an ecodesign strategy (Ahmadi and Tiruta-Barna 2015; Rossi et al. 2016) evaluating the environmental performance of different methods of producing nZVI at laboratory scale, namely the traditional one based on the use of sodium borohydride as reductant and the green synthesis using extracts from natural products or wastes.

The objectives of the work were to evaluate the environmental impacts and the costs of the synthesis process of nZVI by traditional and green methods, which can help to decide if alternative methods of producing nZVI are promising and should be further developed or scale up, leading to more sustainable processes.

2 Synthesis of nZVI

In this work, two methods of producing nZVI were considered: the traditional method using sodium borohydride and the green method using oak leaf extracts (Machado et al. 2013). Oak leaves were selected in this work because of the abundance of oak trees in the Portuguese territory and because of the good properties and characteristics that they presented in the previous tests performed by some authors of this work (Machado et al. 2013, 2015).

2.1 Traditional synthesis of nZVI

The nZVI particles are prepared by mixing equal volumes of 0.2 M $NaBH_4$ and 0.05 M $FeCl_3$ solutions, according to the following reaction (Sun et al. 2006):

$$4\,Fe^{3+}_{(aq)} + 3BH_4^- + 9H_2O \rightarrow 4\,Fe^0_{(s)} + 3H_2BO_3^- + 12H^+_{(aq)} + 6H_{2(g)} \quad (1)$$

The borohydride solution is added slowly into the iron chloride solution with continuous stirring. In order to use the synthesised nZVI for environmental remediation, complementary cleaning operations should be done, such as vacuum filtration and washing with deionised water and ethanol (Sun et al. 2006). In this process, there are generation of wastewater and wastes (paper filters) and their treatment was considered, namely wastewater treatment and incineration of hazardous wastes.

Figure 1 presents the stages of the traditional synthesis method and the inputs and the outputs of the different stages/operations:

2.2 Green synthesis of nZVI

Leaves from oak trees were milled using a normal kitchen chopper. Of milled leaves, 1.8 g is mixed with 50 mL of water and heated at 80 °C during 20 min with continuous stirring. After this stage, 1 mL of extract was mixed with 250 μL of iron(III) solution (0.1 M) to produce the nZVI (Machado et al. 2013). Afterwards, leaves were removed by filtration. Figure 2 presents the several stages of this synthesis method and the inputs and the outputs of the different stages/operations. In this process, the wastes generated are leaves and paper filters and the final disposal considered was municipal waste incineration since composting is out of consideration due to possible contamination of compost with iron and disposal in landfill, in European Union, is nowadays the last option to consider due regulatory constraints.

3 Life cycle assessment

3.1 Purpose and scope

The objective of this work was to perform a life cycle assessment of the two nZVI synthesis methods mentioned before: traditional and green. This study was based on primary data given by experiments/essays executed or available in bibliography and secondary data given by proper LCI data sets available on Ecoinvent. The Ecoinvent database v.3.1 provided data for electricity, $FeCl_3$, $NaBH_4$, paper filter and ethanol production, waste incineration and wastewater treatment. A full list of the applied Ecoinvent processes is presented in Table A1 in the Electronic Supplementary Material. The methodology of impact assessment used was the "IMPACT 2002+" that proposes a feasible implementation of a midpoint in a combined approach to damage, connecting all types of inventory results of the life cycle, through 12 level categories. These categories are then aggregated in four damage categories: climate change, ecosystem quality (aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification and nitrification,

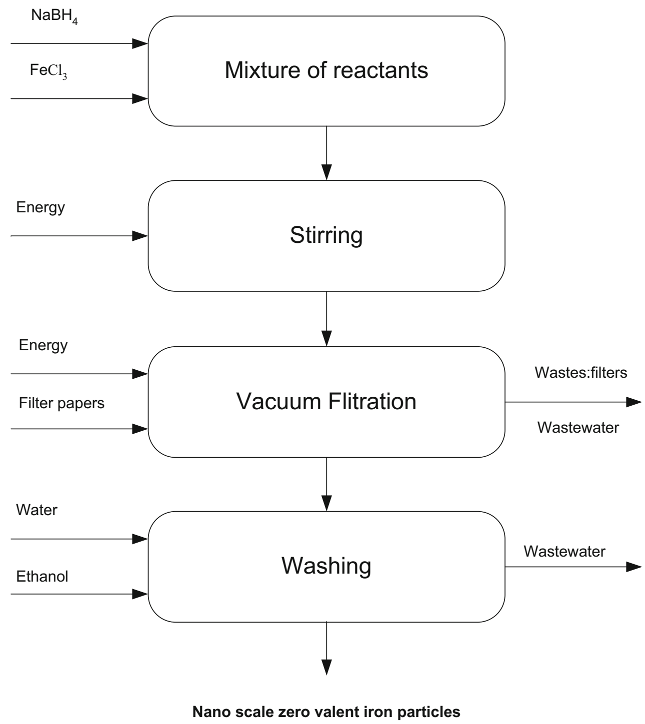

Fig. 1 Traditional synthesis of nZVI

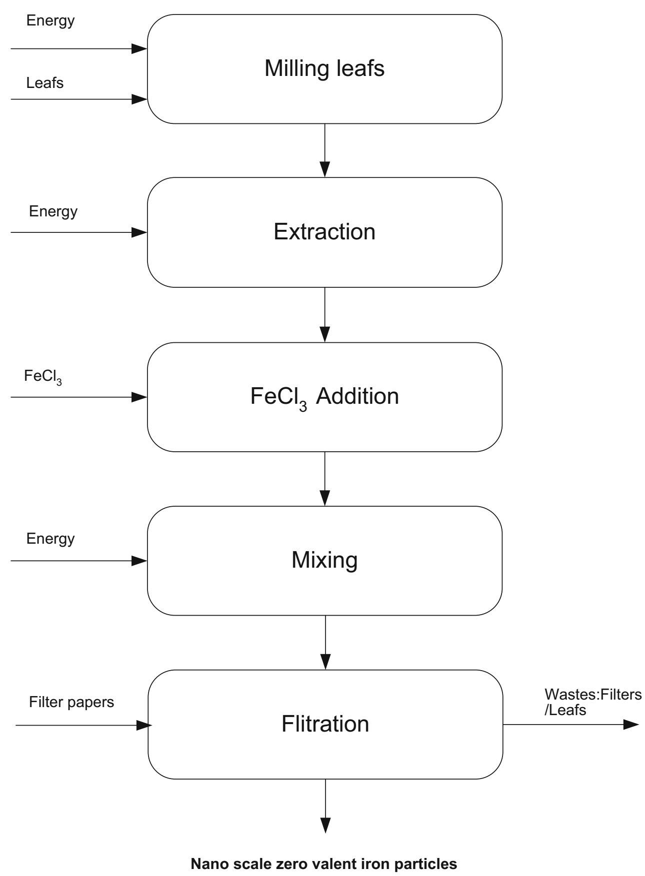

Fig. 2 Green synthesis of nZVI

Table 1 Inventory for chemical synthesis

Stage synthesis process	Input	Output
Mixture of reactants	2.90E−03 kg of $FeCl_3$	
	2.71E−03 kg of $NaBH_4$	
Stirring	1.43E−01 kWh	
Filtration	3.98E−02 kWh	2.49E−03 kg solid waste
	2.49E−03 kg filter paper	7.16E−04 m^3 wastewater
Washing	3.76E−03 kg ethanol	2.01E−04 m^3 wastewater
		1.00 g of nZVI

land occupation), human health (ionising radiation, respiratory effects (inorganics), photochemical oxidation, ozone layer depletion, human toxicity) and resources (non-renewable energy and mineral extraction). One of the advantages of this methodology is that the results are expressed in points due to the normalisation at damage which facilitates calculations. To calculate the global indicator, a default weighting of 1 was considered, meaning that all categories have the same weight. The LCA includes all raw materials and nZVI synthesis, and it was performed with a "cradle to gate" approach: thus, system boundaries end at the synthesis process.

The stages considered for each synthesis method are represented in Figs. 1 and 2, respectively, for the traditional and green methods. Disposal of wastes (paper filters and washing effluents in traditional synthesis method, and paper filters and leaves in green synthesis method) was also considered in this work. For the determination of the ethanol quantity used in the washing process, the relation provided in Sun et al. 2006 was

Table 2 Inventory for green synthesis

Stage synthesis process	Input	Output
Milling (electricity)	1.50E−03 kWh	
Extraction	5.41E−02 kWh (heating)	
	1.35E−02 kWh (losses)	
	9.55E−02 kWh (stirring)	
Reactant addition	2.90E−03 kg of $FeCl_3$	
Mixing (electricity)	1.19E−02 kWh	
Filtration	2.49E−03 kg filter paper	2.83E−02 kg solid wastes (leafs, filter paper)
		1.00 g of nZVI in solution (ready to be used)

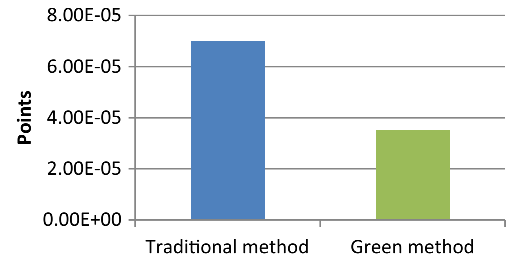

Fig. 3 Total environmental impact of the alternatives for synthesis nZVI

considered and the wastewater generation was calculated taking in consideration the used volume of water and ethanol. The mass of 1 g of nZVI was used as functional unit, and in both cases, full conversion of iron(III) was considered (Machado et al. 2013; Sun et al. 2006).

3.2 Inventory

Tables 1 and 2 present the inventories for the traditional and green synthesis of 1.00 g of nZVI. Initial inventory for the traditional method considered 25 mL of each solution, so the total volume for this method is equal to the volume used for green synthesis.

For the mixing stage in the traditional synthesis, it considered 30 min of stirring (Sun et al. 2006) (considering the use of a magnetic stirrer Breda scientific (Cas.34521) with a power of 20 W).

For the milling stage of the green synthesis method, it considered a time of 3 s for 10 g of leaves (measured) using a Moulinex A320 chopper with a power of 700 W. For the extraction step, the energy necessary to heat the mixture (an aqueous solution) from 15 to 80 °C was calculated, according to the following equation:

$$Q = m \times c_p \times \Delta T \quad (2)$$

where Q is the required energy, c_p is specific heat capacity of

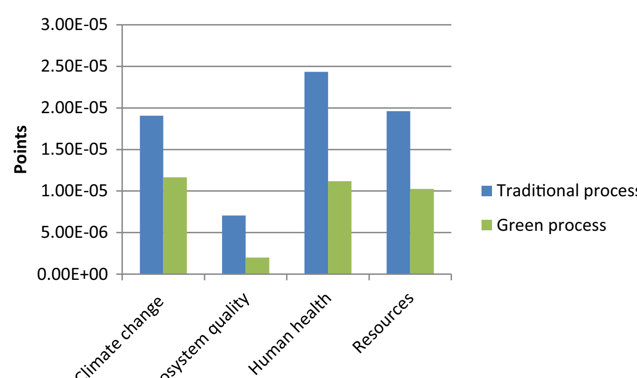

Fig. 4 Environmental impacts by category of damage for each alternative

Table 3 Critical stages/operations in traditional and green synthesis

Traditional synthesis Stage/operation	%	Green synthesis Stage	%
$FeCl_3$ addition ($FeCl_3$ production)	1.7	Milling (energy production)	0.7
$NaBH_4$ addition ($NaBH_4$ production)	43.7	Extraction-heating/stirring (energy production)	80.0
Stirring (energy production)	35.2	$FeCl_3$ addition (FeCl3 production)	3.3
Filtration (energy and filter production)	10.9	Mixing (energy production)	5.9
Washing (ethanol production)	4.7	Filtration (filter production)	2.2
Waste disposal (hazardous waste incineration)	2.0	Waste disposal (municipal waste incineration)	7.9
Wastewater treatment	1.8		

water and ΔT the difference of temperatures. Heat losses were estimated considering an insulating layer and correlations given in Incropera and De Witt (2003). The total energy for heating was calculated by adding Q and the heat losses. This resulted in the consideration of an additional 25% factor in the required energy. Mixing time for stirring was 150 s (for 50 mL).

3.3 Environmental impact assessment

Figure 3 presents the overall environmental impact of the two methods for the synthesis of 1.00 g of nZVI, considering electricity at low voltage for Portugal. As can be seen, the green synthesis presents lower global potential environmental impact, roughly 50% lower than the traditional synthesis. Detailing the environmental impacts by damage categories, it is possible to conclude that traditional synthesis presents higher environmental impacts in all damage categories, especially in human health (Fig. 4).

Analysing contributions inside damage categories, it is possible to conclude that the major contribution for the ecosystem quality category for both methods comes from terrestrial ecotoxicity, with 79.9 and 83.2%, for traditional synthesis and green synthesis, respectively. In this level category, the value for environmental impacts for traditional synthesis is 3.4 times the value for green synthesis. For human health category, respiratory effects (inorganics) are the most important with 87.3 and 82.6% for traditional synthesis and green synthesis, respectively. In this level category, the value for environmental impacts for traditional synthesis is 2.3 times the value for green synthesis. For resources, non-renewable energy is the most important with 99.9% for both methods. In this level category, the value for environmental impacts for traditional synthesis is 1.9 times the value for green synthesis.

Table 3 presents environmental impacts of the several stages/operations for both synthesis methods and processes involved. Analysing data, it is possible to conclude that the most critical stage for green synthesis is the extraction which is related to the production of electricity and that represents 80% of environmental impacts of the synthesis process. For the traditional synthesis $NaBH_4$, addition and stirring are the most critical stages and correspond to 44 and 35% of total environmental impacts, respectively (Table 3).

In fact, $NaBH_4$ production is an important contributor in all damage categories, with a percentage of 38.4% in climate change, 41.1% in ecosystem quality, 49.1% in human health and 43.0% in resources. Thus, considering the background processes involved, it is possible to say that for traditional synthesis, electricity production and $NaBH_4$ production are the principal contributors with 45.0 and 43.7%. All other

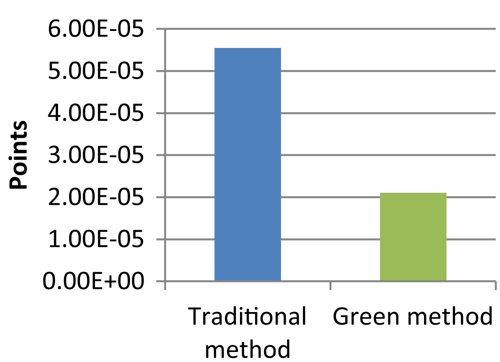

Fig. 5 Total environmental impact of the alternatives for synthesis nZVI (Switzerland)

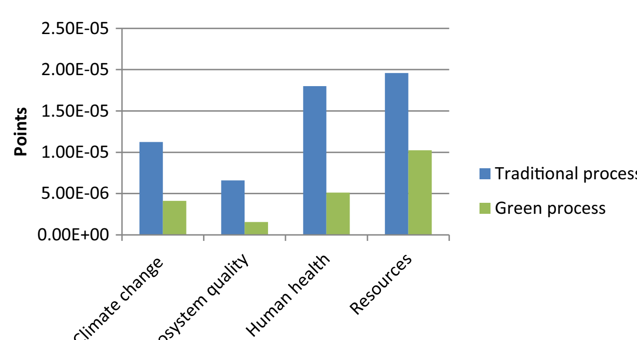

Fig. 6 Environmental impacts by category of damage for each alternative (Switzerland)

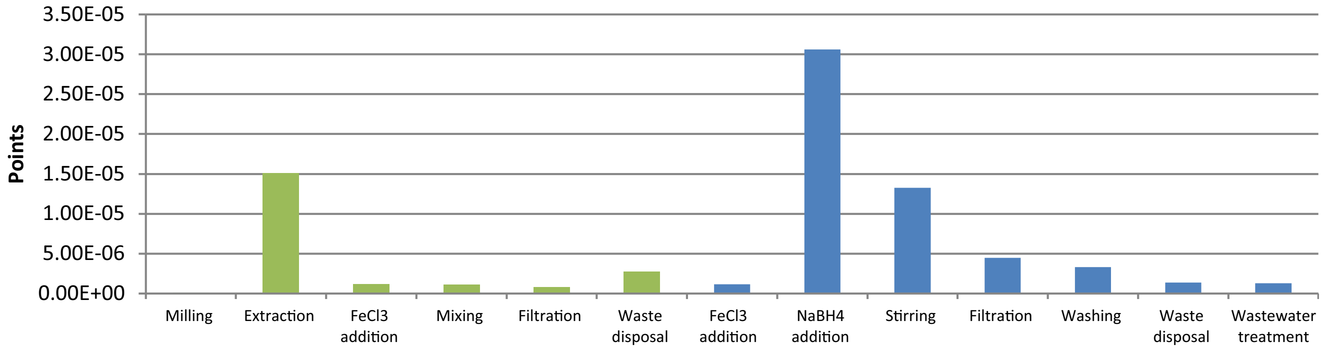

Fig. 7 Environmental impacts of the several stages/operations for both processes (Switzerland)

processes present percentages lower than 5%. Attending to the green synthesis, electricity production is by far the most important contributor with 86.6%, followed by waste disposal (municipal waste incineration) with 7.9%. The remaining processes present percentages lower than 5%.

3.4 Interpretation

After applying LCA to traditional and green synthesis, it was possible to conclude that environmental impacts of green synthesis are 50% lower than the ones presented by traditional synthesis and that they depend mainly on the electricity production due to extraction stage. The environmental impacts of the green synthesis method can be reduced by optimising the extraction stage since it is the hotspot of this method. In this method, the extraction phase was performed at 80 °C but the use of lower temperatures could be considered; however, this change can lead to a decrease on the amount of nZVI produced. Another aspect that could reduce environmental impacts is the electricity production process that in fact could benefit both synthesis methods since electricity production contributes significantly to global environmental impacts of both processes. Electricity mix with high share of renewables and lower share of fossil sources will probably lead to a decrease in environmental impacts in both processes and an even more favourable result to green synthesis since it is very meaningful to this process.

4 Sensitivity analysis

One of the most important tools to quantify uncertainty is scenario analysis which was used in this work. In order to perform the sensitivity analysis, another scenario for the production of electricity was considered. Different countries have different mixes for electricity production and this affects the potential environmental impacts. By the reason mentioned above and because the ecoinvent database was developed by the Swiss Centre for Life Cycle Inventories (Frischknecht and Rebitzer 2005), the environmental impacts were also calculated using electricity at low voltage in Switzerland. The results are presented in Fig. 5 and it is possible to conclude that both synthesis methods present lower environmental impacts when compared to the first scenario and the environmental impact of green synthesis corresponds to 38% of the environmental impact of traditional synthesis. Detailing the environmental impacts by damage categories for the second case, it is possible to conclude that traditional synthesis presents higher impacts in all damage categories, especially human health and climate change (Fig. 6). Data for process of electricity production, Switzerland (CH) was obtained through ecoinvent Version 3 Database.

Analysing the different stages of the synthesis methods, it is possible to detect the critical stages for each alternative. In the traditional synthesis, the critical stage continues to be the sodium borohydride addition (related to sodium borohydride production), and in the green synthesis (represented with a green colour in Fig. 7), the critical stage the extraction phase (Fig. 7).

The difference registered between the Portuguese and the Swiss scenario can be attributed to the different electricity production mixes of the two countries: Switzerland mix is essential based on hydropower and nuclear plants and in Portugal electricity production still uses thermal power plants. With the increasing share of renewable in the mix, the results

Table 4 Cost of nZVI for traditional and green synthesis

	Green process Costs (€)	Traditional process Costs (€)
$FeCl_3$	0.04	0.04
$NaBH_4$	–	0.81
Ethanol	–	0.02
Filter paper	0.06	0.06
Electricity	0.01	0.01
Non hazardous waste disposal	0.00	–
Hazardous waste disposal	–	0.00
Wastewater treatment	–	0.00
Total	0.11	0.95

probably will change to an even more favourable result to green synthesis.

5 Economic evaluation

Besides the environmental analysis, it is important to perform an economic evaluation of both synthesis processes. Prices for reactants, electricity, solid waste incineration, etc. were obtained through market inquiries, and based on this data, the cost for producing 1.00 g of nZVI was estimated and is presented in Table 4.

It is possible to conclude that the traditional synthesis is a much more expensive process that green synthesis (roughly eight times higher) being the sodium borohydride cost the major factor to this difference.

6 Conclusions

The use of nZVI in soil remediation has a great potential so it is important to develop sustainable processes for its production. There are several bottom-up methods to synthesise nZVI being the traditional and green synthesis two of the most common alternatives. It is important to consider environmental impacts and economic factors in earlier stages of methods to account these aspects in research and in development, using tools such as LCA as an ecodesign strategy to verify if alternative methods are promising and should be further developed.

Green synthesis presents lower environmental impacts than the traditional method. The critical stage in the green synthesis is the extraction process which in turn is related to electricity production. An electricity production system based on renewable energy will probably lead to even lower environmental impacts because the environmental impacts due to electricity production will decrease. Portugal electricity mix, for example, still depends on thermal power plants.

In the traditional synthesis, the reactant use, namely sodium borohydride production, is the most critical stage in that process. In the green synthesis, the use of lower temperatures would be a positive factor although the amount of nZVI obtained should be a factor to be considered. The economic evaluation revealed that the traditional synthesis is a much more expensive process than green synthesis.

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