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Comparative life cycle assessment of different synthesis routes of magnetic nanoparticles

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ABSTRACT

Nanotechnology is the manufacture and use of functional structures that have at least one characteristic dimension measured in nanometers. Among the wide range of applications nanoparticles (NPs) may present, they can be used as a catalyst or as carrier to immobilize biological catalysts, such as enzymes. The use of magnetic nanoparticles (mNPs) presents as main advantage over other alternatives the fact that they can be easily separated by the application of a magnetic field, facilitating their recovery from the reaction medium. In parallel with the increasing interest in the production of nanomaterials, there is a general consensus about their potential health and environmental risks associated. This paper aims to perform the evaluation of different synthesis routes considered for the production of mNPs from a life cycle assessment (LCA) perspective. Specifically, different approaches of mNPs synthesis were evaluated; from simple forms such as sterically-stabilized magnetite and oleic-acid mNPs to production schemes that consider the coating of a shell on the preformed nanoparticles such as PEI-coated mNPs and silica-coated mNPs for the increased stability of the nanoparticle. When merely assessing the outcomes from the LCA study, we observed that the manufacturing stage is dominated by the environmental impacts associated to energy and chemical use, especially relevant for the type of silica-coated mNPs. However, the selection of the optimal support for enzyme immobilization must comply with additional requirements such high immobilization yield. According to the results, a compromise solution for the selection of the support is obtained for PEI-coated mNPs, with satisfactory results in the indicators of enzyme immobilization and limited environmental impact. Moreover, this work highlights two main challenges currently encountered with the application of LCA to nanoproducts: lack of comparable reports and data availability, both imply uncertainties associated with the estimation of the environmental impacts of NPs.

1. Introduction

Nanomaterials are defined as materials with at least one characteristic dimension in the range of 1 and 100 nm. Nanomaterials can be natural (e.g., humic and fulvic acids) (Thurman and Malcolm, 1981), incidental to human activity (e.g., diesel emissions, welding fumes) (Peters et al., 2009), or engineered. Engineered Nanomaterials (ENMs) differ from bulk materials in two main characteristics: relative surface area and quantum effects. Firstly, as particle size decreases a greater proportion of atoms can be found at the surface. Hence, nanoparticles have a greater surface area when compared to larger particles and this feature is likely to result in faster rates of chemical reactions as well as changes in strength and electrical characteristics. Secondly, the benefit of nanomaterials is attributed to the quantum nature of energy states at the nanometer scale, which can affect the optical, electrical and magnetic behaviour of matter (Royal Society & Royal Academy of Engineering, 2004). On the contrary, a number of drawbacks are inherent to the production and use of nanoparticles: the complexity of their production scheme and their instability as they can easily undergo transformations. Moreover, their recycling and disposal may be complicated as there is no definite solution for the disposal of nanomaterials.

Most ENMs can be divided into two general classes, depending

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on whether they are carbon-based (e.g., carbon nanotubes and fullerenes) or metal-containing (e.g., Ag, TiO_2, CeO_2, Fe) (Heithmar and Pergantis, 2010). Among the different ENMs, magnetic nanoparticles have received a great deal of attention because of their potential use in various biomedical applications, including contrast agents in magnetic resonance imaging (MRI), magnetic separation and sorting of cells and proteins, immunoassay in pathology laboratories, hyperthermia treatment for cancerous tumors, and targeted delivery of pharmaceuticals and therapeutic genes (Babic et al., 2008; Tsuzuki, 2013). The potential advantage in the use of magnetic nanoparticles (mNPs) over other NPs relies on the fact that they can be easily separated by the application of a magnetic field.

Regarding the synthesis routes of mNPs, they can be produced through a variety of processes based on physical, chemical and biological methods with differing mechanisms, inputs, yields, reaction conditions and nanoparticle size distributions (Willard et al., 2004; Tartaj et al., 2006). Chemical coprecipitation is probably the most common method to prepare magnetic nanoparticles (Laurent et al., 2008). In this method, it is usually necessary to start from a mixture of ferrous and ferric salts suspended in an aqueous alkaline medium that renders into nanoparticles with a broad size distribution (from 4 to 20 nm). Alternatively, other methods are currently being developed to produce nanoparticles with more uniform dimensions. In this regard, water-in-oil (w/o) microemulsion can be considered as it consists of nano-sized water droplets dispersed in an oil phase and stabilized by surfactant molecules at the water/oil interface (López-Quintela et al., 2004). The surfactant-stabilized nano cavities (typically in the range of 10 nm) provide a confinement effect that limits particle nucleation, growth and agglomeration.

Beyond the alternatives considered for the production of stabilized magnetic nanoparticles, which can perform the electrostatic immobilization of proteins, a shell of an appropriate material on the original nanoparticle such as silica, polyelectrolyte and micelles, has been applied for a more stable structure (Gupta and Gupta, 2005). The magnetic core ensures a strong magnetic response and the polymeric shell enables the modification of the surface with target functional groups. Surface functionalization would allow the desired molecules such as proteins to be immobilized by covalent binding on or conjugated to the particles, enabling targeted biological applications such as site-specific markers, bioconjugates and sensors (Subbiah et al., 2010). Most enzymes are covalently attached using their lysine amino groups because of their frequent presence on the protein surface and high reactivity (Brady and Jordaan, 2009).

In parallel with the increasing interest in the production of nanomaterials, extensive research into potential environmental and health implications of their production and use has been developed, particularly given the projections for their widespread incorporation into consumer products. The uncertainty associated with the potential toxicological effects of nanomaterials is yet to be assessed in order to develop specific disposal policies (Alagarasi, 2009). Keller et al. (2013) estimates the release of ENMs from various waste management methods by assuming identical potential of release for all ENMs and applications, due to the absence of case specific data.

According to Grieger et al. (2012), there is a general consensus amongst scientists, researchers and regulatory agencies that the potential health and environmental risks of ENMs should be evaluated over their entire life cycle. Application of Life Cycle Assessment (LCA) to nanotechnology would highlight both the positive and negative impacts of nanotechnology on the environment and it would have to include all aspects of activities during the life of a product 'from cradle to grave', such as extraction of raw materials and resources, production process, use of products, and management of the product including recycling and disposal at the end-of-life stage. By doing so, LCA helps to identify the potential risks associated with nanomaterials in advance to their complete implementation. However, there are inherent difficulties in performing the LCA of nanomaterials. The major obstacles include the uncertainty arising from the immature nature of the technology and markets, the reluctant perspective to provide extensive information on the processes under development and the lack of risk-associated information and characterization factors for LCA impact assessment (Tsuzuki, 2013).

The available LCA studies of ENMs include nanomaterials such as CdTe, carbon nanofibres (CNFs) and nanotubes (CNTs), nanoclay (ONMT, organically modified montmorillonite), nanoscale Pt-group metals, nanocrystaline-Si, Ag, titanium and titanium oxide (Hischier and Walser, 2012; Gavankar et al., 2012; Upadhyayula et al., 2012). The main outcomes from these studies report that both energy and chemicals use during ENM synthesis contribute a significant and often dominant share of total life cycle environmental impacts (Walser et al., 2011; Eckelman et al., 2012). However, the Life Cycle Inventories (LCIs) cannot be classified as comprehensive as they often lack ENM specific data related to the outputs of the processes. Moreover, a considerable variability of the (traditional) inventory items like energy input, material input, etc. was observed (Hischier and Walser, 2012). Regarding magnetic nanoparticles (mNPs), no available LCA reports on the different routes of synthesis were found.

In this paper, different approaches of mNPs synthesis were considered, from the production of sterically-stabilized magnetite and oleic-acid stabilized magnetite to production schemes where the coating of a shell on the preformed nanoparticles is developed to obtain PEI-coated magnetite and silica-coated magnetic nanoparticles. However, not only is necessary to assess the environmental consequences of the different production alternatives of magnetic nanoparticles, but also to demonstrate that they can be used as viable supports for the immobilization of proteins, in this case, the oxidative enzyme laccase.

2. Materials and methods

2.1. Goal and scope definition

The purpose of this work is to evaluate the environmental performance of different routes for the synthesis of magnetic nanoparticles. The assessment is based on real data from the production schemes of mNPs developed by the NanoMag group at the University of Santiago de Compostela. Fig. 1 depicts the four production schemes or scenarios included within the system boundaries of the environmental study. The detailed description of the four routes is detailed in the next section. Both the amount of waste streams produced as well as their treatment were considered identical for the different synthesis routes (i.e. wastewater from washing steps and re-dispersion activities). Their potential variability in terms of composition is beyond the scope of the environmental analysis since no information about them was supplied.

2.2. Description of the production processes

2.2.1. Preparation of sterically-stabilized magnetite (Scenario 1)

In a typical synthesis, $FeCl_3.6H_2O$ (9 mmol) and $FeSO_4.7H_2O$ (6 mmol, molar ratio $Fe^{3+}/Fe^{2+} \approx 1.5$) were incubated in 0.01 M HCl solution with mechanical stirring at 60 °C, following the Massart's method (1981). Ammonium hydroxide solution was added to the mixture, which led to the immediate formation of black magnetite nanoparticles, which will be the basis for the different alternatives

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