

"Green" nanomaterials: synthesis, assessment, and their potential application in soil remediation

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ABSTRACT: The effects of environmental pollution on planetary health have led to a growing interest in implementing sustainable remediation processes, which should ideally be characterized by a high efficiency for the elimination of recalcitrant substances and a null production of cross-pollution. In this ambit, nanomaterials synthesized from green chemistry principles emerge as an alternative for the development of eco-friendly technological strategies. However, this framework of thought is qualitative in nature and not gives minimum criteria for using the term "green" in the field of nanoscience and nanotechnology. This adjective is usually employed to refer to those processes developed through bio-based nanotechnological methods without take in consideration its net ecological impact under out-lab conditions. Nonetheless, biobased synthesis represents a promissory technology to obtain eco-friendly nanomaterials with greater suitability to be applied in strategies of environmental remediation. Particularly, in the previous context, iron-based nanomaterials are able of reducing the concentration of a wide variety of pollutants individually or by synergy processes with other bioremediation agents. By the above, it is expected that the release into the environment of iron biobased nanomaterials will increase over time, and therefore, it is of interest to establish the potential interactions that they can undergo with the soil components (e.g., soil atmosphere, soil solution, humified organic matter, and minerals, among others). This review is focused on "green" nanomaterials and includes not only fundamental and synthetic aspects, but also, a review of the quantitative assessment from a green chemistry and sustainability criteria. In addition, the potential application of biobased nanotechnology into soil remediation, using as model iron-based nanomaterials, is reviewed, and discussed. Finally, it is relevant to clear that this document is based on two review articles and a book chapter in which the different aspects previously indicated are shown and analyzed in greater detail.

INTRODUCTION

Since the nineteenth century, humanity has presented a constant demographic, industrial, and urban growth, which has led to an intensification in the extraction of natural resources, as well as in the use of anthropogenic substances for the generation of efficient production mechanisms. These processes have contributed to economic growth, to the improvement of the quality of life, essential products for human communities, and greater accessibility to food in terms of quantity and quality.¹⁻³ However, the lack of a specific strategy, policies, and regulations, regarding the final disposition and environmental considerations of the products, by-products, and wastes, led to the release into the environment more than three million metric tons of toxic substances and pollutants per year.¹ In this way, a remarkable proportion of contemporary soils and aquifers have a wide variety of polluting substances, both natural and anthropogenic in origin, including heavy metals, hydrocarbons, agrochemicals, pharmaceuticals, and personal care products, among others.⁴ Due to this situation, a wide range of pollutants are currently present in water bodies and soils; however, since soils are not a fluid phase, conventional remediation techniques commonly used for aqueous systems are not applicable or easily adaptable to them.^{5,6}

As a result of the above, for remediation purposes, soils represent a challenge yet to be resolved. Thus, it is well-known that soils are naturally reservoirs for inactivating polluting species due to their chemical speciation. In soils, for example, organic components can interact, depending on their chemical structure, with pollutants by electrostatic interactions with ionic groups, by dispersive interactions with hydrophobic structural segments and surfaces, by ion-dipole interactions with polar groups, and by the formation of new chemical species via covalent or coordinating links.⁶ While inorganic components, primarily clays, dissolved ions, and oxygen, can present electrostatic interactions, redox reactions, and adsorption processes on their surface and interlaminar region, altering chemical nature, properties, and the microstructure of clays.⁶ Chemical and structural changes in components of soils affect pollutant's bioavailability, lead to variations in cation exchange properties, the polarity of components, retention of solutes, affect the microbial population, and transport of water and nutrients, among others.^{6,7} In addition, pollutants can also be mobilized through the soil horizons hydrologically by the percolation of the soil solution, runoff, and erosion, generating water bodies contamination.⁸⁻¹²

Alteration of environmental systems, resulting from multiple human activities, has produced the growing

need to advance in the development of efficient remediation strategies able to face the heterogeneity and complexity of the soil by sustainable processes.¹³ Thus, for the development of soil remediation techniques, it is important that their implementation does not produce secondary contamination or implies an excessive use of energy.¹⁴⁻¹⁷ In this context, the use of so-called green nanomaterials for remediation processes has emerged as a promising sustainable alternative because they present the ability to diffuse inside of structures that are not easily accessible to macroscopic materials (e.g., soil porous structures), but also, these materials have the potential to interact intimately with pollutants through various mechanisms including adsorption, oxidative transformations, and catalytic processes.¹⁸⁻²¹ An advantage of them is the possibility to be manufactured taking into consideration sustainability and green chemistry criteria. However, these approaches correspond to a qualitative approximation grouped into the concept “green”; in consequence, there is currently a subjective and ambiguous designation associated with the use of this term.²² Therefore, build a solid conceptual framework that objectively supports the rational, sustainable, and eco-friendly synthesis of biobased nanomaterials, which are designed for applications involving their release in natural environments, an analysis of their scope, advantages, and limitations becomes a great relevant goal. In recent years, researches related to the development and assessment of these nanotechnological systems in environmental remediation have significantly increased, mainly those related to iron-based nanomaterials (FeNMs), including both individual and hybrid materials or processes, e.g., through processes including bioremediation and nanoremediation, sequential configurations and/or in metabolic biostimulation, polymer-based nanocomposites as adsorbents or active surface, ferromagnetic fluids based on magnetic particles, among others.^{1,17,23,24}

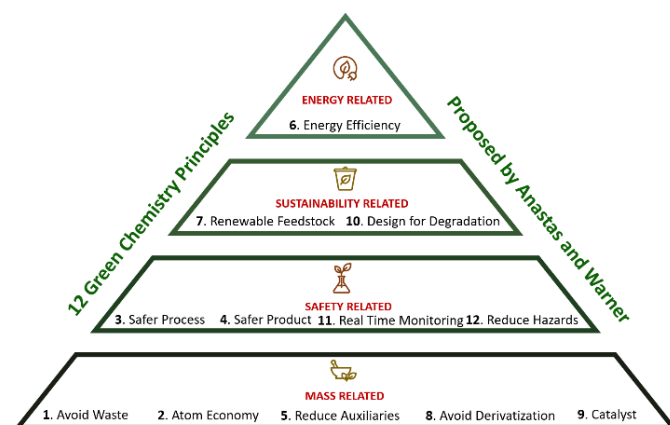


Figure 1. The twelve principles of green chemistry.²⁵

This review is focused on “green” nanomaterials and includes not only fundamental and synthetic aspects, but also, a review of the quantitative assessment from a green chemistry and sustainability criteria. In addition, the potential application of biobased nanotechnology into soil remediation, using as model iron-based nanomaterials, is reviewed, and discussed. Finally, it is relevant to clear that this document is based on two review articles and a book chapter in which the different aspects previously indicated are shown and analyzed in greater detail (see section: Associated Products).

GREEN NANOMATERIALS: SYNTHESIS AND ASSESSMENT METRICS

Green nanotechnology

Green Chemistry is a fundamental concept and a framework of thought based on environmental sustainability and into the development of eco-friendly technologies and processes. Its main ideas are described on the so-called green chemistry principles (see Figure 1).^{26,27} In this way, green chemistry allows advancing in the environmental optimization of parameters associated with chemical transformations by eco-innovation and creativity in order to redesign or replace traditional processes.^{3,23,28}

In this way, the concept “green nano” emerged by extrapolating green chemistry principles to this specific area of science and technology.²⁹ For this reason, the term green nano refers to nanoscience (NanoSci) and nanotechnology (NanoTech) with an environmental focus in its design, application, and final disposal; therefore, it is an area of knowledge based on the generation of sustainable and safe nanomaterials.^{29,30} This sustainability framework implies that the process's analysis includes aspects related to reagent selection, design of synthetic procedures in terms of mass and energy, analysis of potential application, disposition in the end-life, analysis of risks and environmental consequences taking into consideration the entire process.^{31,32} Besides, green nano seeks to advance in the development of regulatory frameworks and procedures allowing standardize the use, practices, and functional and structural analysis of green nanomaterials for environmental applications.^{23,33} The twelve principles of green chemistry applied to NanoTech and NanoSci fields are summarized below:

- **Principle one:** Avoiding the production of waste.^{27,34} In relation to this point, in NanoTech, significant progresses have been performed in the implementation of efficient synthesis, able to obtain monodisperse and stable nanomaterials. In particular, the use of natural extracts and nanobiofactories using a reduced quantity of reagents and avoiding the generation of by-products are highlighted.³⁵

• **Principle two:** The atom economy is a concept recognizing the fact that the synthetic efficiency is closely related to the inclusion of the highest number of atoms of all the reagents in the products.³⁶ In this way, NanoTech presents multiple limitations in term of massive production of nanomaterials; by instance, conventional physical syntheses are characterized by low material conversion with a high polydispersity of size and shape compared with chemical methods, which are characterized by the high production of wastes and elevated use of reaction auxiliaries like solvents, stabilizing agents, surfactants, etc.^{37,38} In contrast, the implementation of post-synthesis methods, and bioreactor-based synthesis have been described as methods able to produce monodisperse nanoparticles with a homogeneous morphology and a lower environmental impact.^{33,35,37}

• **Principle three:** Safer synthetic processes. This principle is based on premise that experimental design must consider all possible parameters of the process, including aspects related to the generation of adverse effects on planetary health.³⁹ In Nanotech, many advances have been directed towards the trans-materialization of dangerous reagents such as the replacement of strong reducing agents by safer alternatives such as aqueous extracts from biological systems like plants, algae, and bacteria.³³

• **Principle four:** Safer products. The use of molecular or smart design, in order to prevent adverse interactions of products with living beings and the environment, is an excellent strategy to decrease the risk and dangerousness of products with great potential to be massively produced for their introduction in the market.³⁴ To achieve this goal, the availability of information is an essential aspect that should be remedied for all actors in the field of NanoSci and NanoTech. Some examples are the generation of libraries of data and properties related to structure-activity relationships about risks of nanomaterials, cooperative work for the creation of access-free data repository by web platforms, and promotion of open-access scientific journals with a low cost, non-profit, financed directly by government entities or by special projects. However, due to the wide variety of nanomaterials, and the fact that their properties are not only a function of its composition, but also depending on its shape, size, and coating agent, in the vast majority of cases the available information does not allow generalizations about the environmental fate.^{16,33,40,41}

• **Principle five:** Avoiding the use of auxiliaries. This principle refers to reducing of solvents used during synthesis and purification, or if not possible, to promote the use of those solvents that do not present an environmental risk, being the use of aqueous media always the most appropriate option.^{27,31} The use of water-soluble precursors and alternative purification processes such as centrifugation and the use of green solvents are

some examples of the implementation of this point in NanoTech.^{35,42,43}

• **Principle six:** Energy efficiency. By this principle is sought reducing the use of conventional sources of energy based on fossil fuels, dirty energy (e.g., combustion-based energy), and any energy form directly associated with the generation of greenhouse gases.³ In concordance with the above, nano-synthesis processes can be carried out at room temperature and atmospheric pressure; in this area, the implementation of alternative energy sources such as microwaves and ultrasound has been proposed.⁴³ But also, the use of biogenic and bio-based synthesis represents a promising alternative since it allows to carry out most of the synthesis processes near to ambient pressure and temperature conditions.^{22,34,35}

• **Principle seven:** Use of reagents from renewable sources. This principle is directly represented in bio-based synthesis because the use of biomolecules and renewable biological systems allow to obtain a wide diversity of nanomaterials, with different biological, catalytic, and optical properties.^{34,42,43}

• **Principle eight:** Avoiding derivatization and minimizing reaction steps. The multi-step processes and derivatization produce a greater use of chemical reagents and decrease the overall atomic efficiency of the process.³⁴ In this area, NanoTech has advanced in processes of synthesis and surface functionalization of nanomaterials by one-pot strategies, preferably directed towards the synthesis of pure substances or easy purification.^{34,35}

• **Principle nine:** Catalysis. This principle is based on the use of catalysts to favor the efficiency and selectivity of chemical reactions.^{34,44} In this context, nanomaterials emerge as the ideal catalysts due to their high surface area and chemical reactivity. However, in processes based on catalytic strategies should be avoided the residuality in the final product and the use of highly toxic catalysts.^{33,34}

• **Principle ten:** Design for final disposal. This principle implies the final disposal of the product in such way that it can be recycled, reused, recovered, or biodegraded.^{31,34} In NanoTech, predictive tools for design, recycling, and recovery of products have been designed, these are based on the implementation of computer programs to establish the Life Cycle Analysis (LCA) of nanomaterials.^{31,34,45}

• **Principle eleven:** Real-time monitoring. Analytical tools allowing the *in-situ* monitoring of reactions and processes are highly desired, these should permit the identification of potential pollutants and associated risks with them.^{34,44} In this context, nanomaterials have been used to develop more sensitive monitoring tools through the interaction and response of the surface plasmon resonance of the nanoparticles. However, their small size, low concentration, and high reactivity, that supposes a rapid change at the moment of being

released into the environment, represent a limitation for its monitoring in uncontrolled environments.^{33,46}

• **Principle twelve:** Prevention from implementing safer processes. This principle is related with the accident prevention by using of inherently safer substances.^{29,34} At present, significant advances have been made in the transmaterialization of reagents for obtaining of nanomaterials with properties analogous to those synthesized by traditional methods; however, in some cases, this is not possible because metallic precursors with non-sustainable extraction methods and inherent toxicity are required.^{3,33} However, decreasing of the risk of exposure by the production of nanocomposites, thus, it is possible to prevent the direct release of the nanomaterial into the environment as a result of washing, or diffusion processes.^{21,35,47}

Green synthesis of nanomaterials

Green synthesis can be defined as any process developed using taking into consideration the green chemistry principles. Nevertheless, the incorporation of all the principles is a chimerical objective, and therefore, usually only some of them are satisfactorily included in the design. In consequence, it is concluded that the development of fully sustainable synthesis or processes is an iterative methodology using the precepts of green chemistry as a purpose for innovation.²⁸ Though many synthetic procedures are not entirely designed under the principles of green chemistry, it is possible that they are eco-friendlier than their predecessor processes, and therefore, “greener” processes. In this case, the adjectivization of “green” emerges as a result of an improvement that contributes to the desired goal. The above is a resource used many times for the promotion of investigations, working lines, and results by many researchers. Therefore, chemical reactions can present minor or major qualitative approximations to the green chemistry, however, the above does not imply that these

processes do not represent an environmental and health risk.

In the same way, the obtaining nanomaterials through plant biomass, microorganisms, and biomolecules (i.e., biobased synthesis), has emerged as the approach most in line with green chemistry parameters. These synthetic pathways are characterized to be a bottom-up process, usually carried out in one-pot systems (principle 8), using renewable and safe raw materials (principle 3, 7, and 12), under conditions of ambient pressure and room temperature or under 200 °C, which avoids or diminishes the excessive use of non-renewable energy sources (principle 6), and by using of water or alcoholic solutions as the reaction medium (principle 3, 5, and 12).^{48,49}

On the other hand, nanostructures with different morphologies, sizes, surface charge, and functional properties through *in-situ* and/or *ex-situ* synthetic procedures can be obtained from living biomolecules and organisms, using metabolic pathways or biomolecules present in different living entities, including bacteria, yeast, and viruses, and higher organisms such as multicellular algae, fungi, and plants (see Figure 2).^{15,18,20,24} Due to the simple propagation of plants, and their wide phytochemical and phylogenetic diversity, the simple extraction capacity of its molecular components through innocuous solvents, and the possibility of using different tissues such as pulps and peels of fruits, leaves, roots, seeds, and flowers, among others, in this sense *ex-situ* plant-based methods are the most widely biosynthetic strategy (see Table 1).^{18,33,35,50-53} In addition, plant-based synthesis compared with those using microorganisms tends to be more efficient in terms of quantity and time, demanding simpler conditions than those required to maintain the proper nutrition, purity, and optimal growth conditions of the microbiological cultures (e.g., lighting, pH, temperature, aeration, energetic source, among others).^{18,51,52}

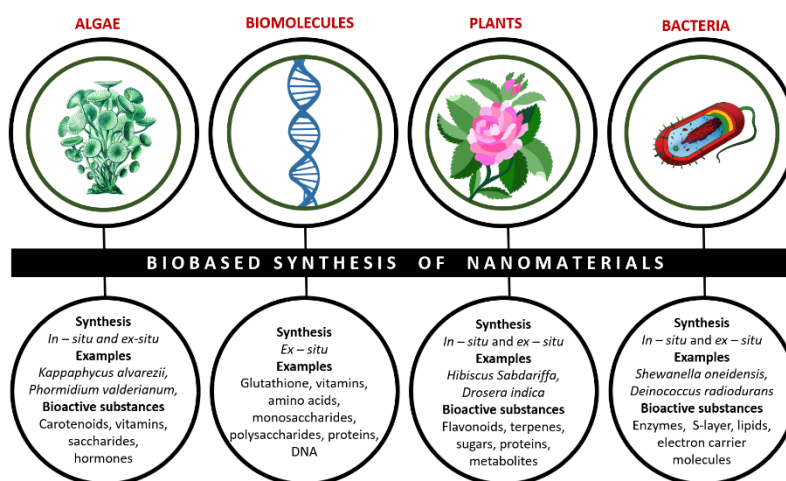


Figure 2. Some of the biological systems and biomolecules used for the synthesis of nanomaterials.⁵⁴

Table 1. Examples of bio-based synthesis of nanomaterials employing diverse plant tissues.

Nanoparticles	Plant tissue	Remarks
FeO (30–100 nm)	<i>Avicennia marina</i> flower	The extract was obtained using an aqueous system boiled for 5 minutes. A FeCl ₃ solution was added to the extract to obtain honeycomb morphology nanoparticles. ⁵⁵
Ag	<i>Nigella Sativa</i> seed	Seeds were macerated and dissolved in an aqueous medium, boiled for 20 minutes, cooled, and filtered. AgNO ₃ 1 mM was added, and the system was heated at 80 °C for 2 hours. Silver nanoparticles with catalytic activity in the degradation of the Congo Red dye were obtained. ⁵⁶
	<i>Ferula persica</i> root	Roots were collected, dried and macerated, double-distilled water was added, and system was heated at 100 °C for 15 min. Later, AgNO ₃ was added to obtain Ag nanoparticles. Nanoparticles showed lower phytotoxicity on the germination of <i>Matricaria chamomilla</i> and <i>Ocimum basilicum</i> , compared to Ag nanoparticles obtained by traditional methods. ⁵⁷
	<i>Allium cepa</i> peels	Peels were sanitized, segmented, placed in an aqueous medium, boiled for 10–15 minutes, and filtered. AgNO ₃ was added to the extract for the obtaining of nanoparticles that showed antibacterial activity against <i>Salmonella typhimurium</i> and <i>S. aureus</i> . ⁵⁸
ZnO (< 50 nm)	<i>Eriobotria japonica</i> seed	Seeds were dried at 50 °C for 24 hours, macerated, placed in an aqueous medium, and heated at 40 °C for one hour. Supernatant was mixed with a solution of zinc acetate and heated at 60 °C for two hours, at this time the system was centrifuged and ZnO nanoparticles obtained were washed with ethanol. These nanomaterials showed antibacterial activity against <i>S. aureus</i> . ⁵⁹
Co ₃ O ₄ (13.2 nm average)	<i>Trigonella foenumgraceum</i> leaves	Leaves were collected, sanitized, dried at room temperature, and macerated. Extract was obtained using an ethanolic medium at 30 °C for 12 hours. The extract was filtered, and CoCl ₂ ·6H ₂ O (0.1 M) was added, in an alkaline medium, the system was heated at 80 °C, centrifuged, subjected to heating at 500 °C for 2 hours, and dried at 100 °C, for finally to obtain the nanomaterial. ⁶⁰

The general *ex-situ* synthesis procedure consists, in the first instance, in determining the plant and the respective tissue to be used. This biomass is collected and sanitized, subsequently dried and macerated, then the particles obtained are placed in aqueous or alcoholic solutions and, usually, it is subjected to heating to carry out the extraction of the biomolecules, even in some cases, the raw extract can be used. After, dissolution is filtered and the filtrate is used to carry out the synthesis, which is commonly performed under room pressure and temperature conditions.^{61–63} In this stage is performed the evaluation of structural characteristics and the optimization of synthesis parameters.

The capacity of plants to carry out the synthesis of nanomaterials is associated with its varied biochemical composition, since this vegetal material has a wide variety of chemical compounds, including lipids, polysaccharides, proteins, vitamins, nucleic acids, aglycones, polyols, pigments, steroids, flavonoids, terpenoids, alkaloids, saponins, polyphenols, peptides, resins, proteins, phytohormones, among others.^{18,22,35,51,64–68} These compounds contain in their structure functional groups like aldehyde, ketone, alcohol, and/or thiols, allowing to carry out chemical reactions of reduction-oxidation and/or stabilization processes of nanoparticles during the synthesis reactions.^{22,35,48,51,64,65} This is the reason why one same

plant species allows the synthesis of nanomaterials of different nature. Such is the case of the plant *Azadirachta indica* (Neem), which has been used to synthesize a wide variety of metal-based nanoparticles. For example, Sharma et al. (2017) synthesized CeO₂ nanoparticles by extract of Neem leaves, obtaining nanomaterials with spheric morphology, an average size of 10 - 15 nm, and the ability to effect photocatalytic degradation of the Rhodamine B dye in aqueous solution, with a yield of 96 % in two hours.⁶³ On the other hand, Abbas et al. (2020) performed the synthesis of silver nanoparticles (AgNPs) and copper nanoparticles (CuNPs) employing an extract of Neem leaves, both nanomaterials presented adsorption capacity of the aromatic hydrocarbon naphthalene until to 98.81 %.⁶¹

On the other hand, small variations in the plant extract concentration, the amount of the nanomaterial precursor, the temperature, or the pH conditions provide the ability to generate nanomaterials with different morphology, size, and biological properties, being this an aspect of relevance for the scientific community.¹⁸ For example, during the synthesis of gold nanoparticles (AuNPs) using an ethanolic extract from leaves of *Artemisia dracuncululus*, it was evidenced that, by increasing the extract concentration, nano-triangles with a smaller dimension were obtained (80 – 130 nm for

3 %, 40 – 75 nm for 4 %, and 35 – 50 nm for 5 %). Respect to the concentration of the metallic precursor, it was determined that at concentrations between 0.05 – 0.28 mM, spherical nanoparticles were obtained; while at 0.50 mM the nanoparticles showed triangular, hexagonal, and spherical morphologies, and at 1.00 mM, the morphologies observed were triangular, hexagonal, and spherical, but with a greater dimension than those obtained with 0.50 mM. Respect to pH, in the values of pH between 2.8 – 4.0, nano-triangles were obtained, which were losing their morphological definition as pH was increased until pH 5.0, where it was evidenced that the particles obtained were spherical.⁶⁹

Having discussed the significant advantages of the biobased synthesis of nanoparticles, in terms of versatility, and operational simplicity, it is necessary to indicate that the reproducibility of the results of these synthetic processes is an open and in development issue. The point of debate arises from the sensitivity of the plant-biobased synthesis to the chemical composition of the reaction medium, which is difficult to guarantee if one takes into account that concentration of phytochemicals in plant material presents a significant natural variability because it is conditioned by nutrition, lighting, phylogenetics, the plant growth stage (e.g., seedling, blooming, senescence, etc.), climatic and geochemical conditions, potential impurities, as well as interactions with the environment (e.g., physical or biological stressors, allelochemicals, plant-rhizosphere interaction, among others).^{24,35,70}

Although plant-based synthesis is a well-known alternative to achieve the objectives of green nano, the fact that most of the scientific publications do not use quantitative parameters to establish its net ecological effect, the scarce information on net energy consumption and on yield in the conversion of raw materials lead to that these processes present little rigor about their real benefit in terms of their ecological impact.^{29,52,70,71} In the scientific literature, reactions denominated to be green can be easily found, however, biosynthetic approaches are based only in some principle of green chemistry (usually, the principle seven); however, these do not consider the LCA of the nanomaterial, and even, in some cases, toxic reagents are used into stages of purification, a high energy intensity is used during process of purification, or a significant number of wastes is produced.^{34,60,72} By the above, it is pertinent to establish that not all processes using nanobiotechnology or bio-based synthesis are consistent with the methodological framework of green chemistry. It is clear that the use of renewable raw materials does not guarantee that the ecological impact of the process is less than that produced by classical procedures. From this analysis, it is inferred that, since there are no minimum criteria to classify a synthesis procedure as a green process, the denomination of a synthesis using this label can be imprecise and even

arbitrary; in consequence, it is clear that exist an inherent difficult to objectively compare, in terms of sustainability, the nanomaterials-biobased synthesis respect to conventional synthesis. Therefore, this situation evidences the necessity to apply sustainability metrics in the nanomaterial synthesis in order to have objective comparison tools.^{34,53,70}

Sustainability metrics applied to green nanomaterials

The implementation of the green chemistry approach in the area of nanomaterials and other technologies, both emerging and well established, can be an intricate process with a considerable degree of complexity since green chemistry is mainly a qualitative strategy, this means that there is a lack of a universal metrics and minimum designation criteria to apply the concept “green” to a chemical process.⁷³⁻⁷⁶ At present, there is no consensus on how to transform the principles of green chemistry into quantifiable metrics able to compare processes and quantitatively identify the aspects to optimize in a synthesis.^{76,77}

The above has led to the need to adopt and develop quantifiable parameters that allow quantitatively establishing the degree of green, or sustainability, in a chemical process, which can be used as tool to obtain an objective and quantitative description about potential environmental impact of synthesis methodologies. The environmental impact is an intuitive concept and the more common criterion taken into consideration in many researches, however, its application have been scarcely implemented for nanomaterial synthesis in out-lab studies and under non-controlled conditions; therefore, factors associated with the degree of material conversion through concepts like the atomic efficiency, the ratio of residues to the product, the energy efficiency, as well as holistic approaches focused on LCA have been proposed as a first approximation for the quantification of impact and risks of the processes on environment and human health.^{36,73,77-79} In contrast, when these parameters are evaluated in the synthesis of nanomaterials, they are not applicable in an ideal way due to the inherent polydispersity of nanomaterials and the difficulty for the establishing stoichiometric relationships among their components.^{78,80} Pitifully, the absence of the necessary information in most scientific articles is frequent, and therefore, to define vital aspects concerning to the application of twelve principles of green chemistry using prospective studies or meta-analysis is not always feasible, or rather, it is limited by lack of data. Therefore, the use of metrics is not a common practice within many research teams. The analysis of the results usually focuses on the characteristics and properties of the product, the methodology in terms of its effectiveness to achieve a synthetic purpose, and the use of “green” in a wide

number of publications is interpreted, in the practice, as a synonym of biobased or nanobiotechnological synthesis. Therefore, it is clear that there is still a significant way forward to bring the concepts of sustainability and green chemistry beyond simple academic irreflective discourse. Other aspects hindering the application of metrics in nanomaterials are the lack of standardization of synthesis procedures, characterizations, evaluation of toxicity, and environmental impacts in the field of NanoTech.^{71,81} Undoubtedly this panorama has led to the scientific community to seek optimizing and adopting well-known metrics from green chemistry in order to apply them to the making of nanomaterials. In this way, the metrics most widely used are the E-factor and LCA.^{71,78,81} These are described below.

E-factor is a parameter associated with the first and second principle. It is based on the relationship between the mass of waste generated in the synthetic process respect to the product mass.⁸² This quotient is described by Equation 1 and allows to establish both a partial and global perspective about the production of waste in one-step and multi-step synthetic processes.⁸³

$$E\text{-Factor} = \frac{\text{Mass of waste (kg)}}{\text{Mass of product (kg)}} \quad (1)$$

E-factor has been used in the field of nanomaterials to establish a correlation between the amount of waste generated respect to different classes of materials.^{30,83} By instance, some authors have been determined the E-factor of various synthesis of purified nanomaterials (see Table 2). It is possible to observe from values in Table 2 that the nanotechnological method based on starch-glucose synthesis presents one of the highest E-factor values (29600), what would make this synthesis a

process that is not in concordance with principles 1 and 2 of green chemistry, therefore, under this perspective, to denominate this process a “green” nanosynthesis because it is based on the use of biomolecules is clearly inappropriate. In contrast, according to Table 2, the synthesis of gold nanoparticles carried out using the bioreactor presents the lowest value of E-factor for AuNPs; from this perspective, biogenic synthesis method is more sustainable than the other methodologies to obtain gold analog nanomaterials in term of residues production, however, results should be carefully analyzed, and generalization should be avoided.³⁰ Note that E-Factor must be calculated for each methodology and interpreted according its context with an objectively delimited scope. The above reinforces the fact that biobased nanotechnology is not *per se* a “green process”.³⁰ In contrast, it is interesting to highlight that the one of the lowest value of E-factor has been obtained for chemical vapor deposition methods for synthesis of carbon nanotubes, a method that has been considered by some authors to be not very eco-friendly due to its energy intensity, which usually implies the generation of secondary pollutants (i.e., greenhouse gases and unsafe wastes), therefore, a limitation of E-factor is clearly evidenced, i.e., E-Factor does not consider the dangerous of wastes. It is well-known that a small quantity of wastes should not be understood as in terms of a low dangerous since some wastes are highly toxic and eco-toxic at very low concentrations.^{26,34,36} On the other hand, a low value of E-factor can be associated with the material recovery of a large part of the reagents used in the process, such as the case of nanosilica fibers (E-factor = 15) obtained by Maity and Polshettiwar, a process with a recovery of 70 % of the xylene used as the solvent, 88 % of the CTAB surfactant, and 92 % of the ethanol used in washing and extraction protocol.⁸⁴

Table 2. E-factor for several syntheses of nanomaterials.^{30,83,84}

Nanomaterial	Synthesis strategy	E-Factor
Gold nanoparticles	Chemical reduction and stabilizing with thiolated ionic liquids	99400
	Reduction and stabilization with starch and glucose biomolecules	29600
	Chemical reduction and stabilization with phosphines	19200
	Chemical reduction and stabilization with thiols	3320
	Use of <i>Medicago sativa</i> as a biological reactor	163
Carbon nanotubes	Synthesis by chemical vapor deposition	170
Nanosilica fibers	Hydrolysis-polycondensation method	15
Fullerenes	By benzene-oxygen flame	950
TiO ₂ nanoparticles	Synthesis by hydrolysis-calcination	17800
	Titanium isopropoxide and water	7.2
Mesoporous silica	Making using triblock copolymers	3400
	Making using ionic and neutral-surfactant template	250
	Making using liquid-crystal templates	90

On the other hand, LCA seeks to identify the parameters to optimize in the generation of processes with a minimum amount of waste, material efficiency, and low impact on public and environmental health.⁸⁵⁻⁸⁷ This

metric emerges as a quantitative parameter of ecological impacts that holistically covers the processes, from a systematic and iterative approach. Though the LCA has been accepted as the complete tool for evaluating the

sustainability of a process, it is considered an improper approach to evaluate emerging technologies that do not have robust data for the construction of the life cycle impact assessment, being this the case of nanotechnology products, nevertheless, at present the LCA has been identified as the most suitable metric for the analysis of the integral ecological impact of nanomaterials.^{36,71,77,88-90}

In the field of green nanomaterials, LCA has been used to compare the net sustainability of synthetic processes of nanostructures with similar chemical composition through different methodologies, including conventional physical and chemical synthesis and those based in plants and biomolecules. In this context, Pourzahedi and Eckelman performed a cradle-to-gate LCA for the synthesis of silver nanoparticles from a functional unit of 1 kg of nanomaterial.⁹¹ The synthesis methods by chemical reduction included the use of sodium citrate, sodium borohydride, ethylene glycol, and starch (hydroxypropyl starch), whereas physical methods were flame spray pyrolysis, arc plasma, and reactive magnetron sputtering in Ar-N₂.⁹¹ Results showed that the flame spray pyrolysis method is a synthesis with the most significant environmental impact in all categories, except fossil fuel depletion, where the ethylene glycol-based method is the most harmful. In addition, results allow determining that the synthesis based on starch presents a lower ecological impact compared to the flame spray pyrolysis method in all aspects, in addition, its contribution is lower than 50 % in terms of acidification, eutrophication, and human health impact (See Figure 3).⁹¹ However, it is relevant to note that the biomass-based method presents higher values for all categories regarding the arc plasma method, which is expected to have a more significant environmental impact due to its energy intensity. In this way, it was possible to establish that the parameters that allow defining a synthesis as eco-friendlier are relative and depend on the strategies used to carry out their comparison.

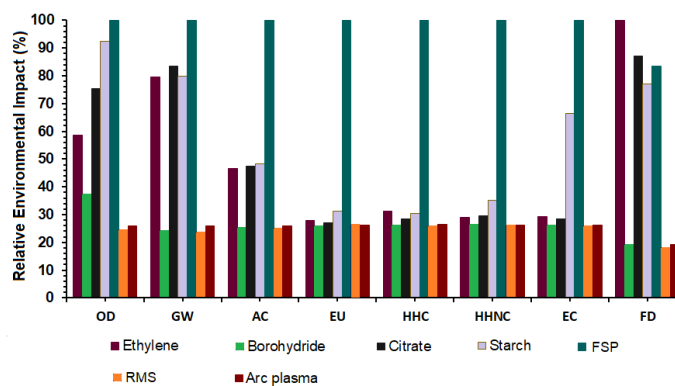


Figure 3. Ecological impact of seven different Ag nanoparticles synthesis (Adapted from Pourzahedi and Eckelman (2015)). OD refers to ozone depletion, GW to

global warming potential, AC to acidification, EU to eutrophication, HHC to human carcinogenic health, HHNC to human non carcinogenic health, EC to ecotoxicity, FD to fossil fuel depletion.²⁵

Compared with the previous example, the research carried out by Marimón-Bolívar and González on synthesis based on biomolecules showed a more sustainable approach in all the ecological impacts evaluated.⁹² This analysis was carried out through a cradle-to-gate LCA. Methodologies compared were: (i) the synthesis of magnetite using glutathione as a reducing and stabilization agent and, (ii) a conventional co-precipitation approach. Results allowed to establish that the biological method presented one or more orders of magnitude lower than the conventional methodology in terms of its impact on climate change, global warming, fossil and water depletion (see Figure 4).⁹² Thus, the biobased alternative emerged as the most sustainable method in this reference framework, which justifies by quantitative aspects that the authors denominate this method as a green synthesis.

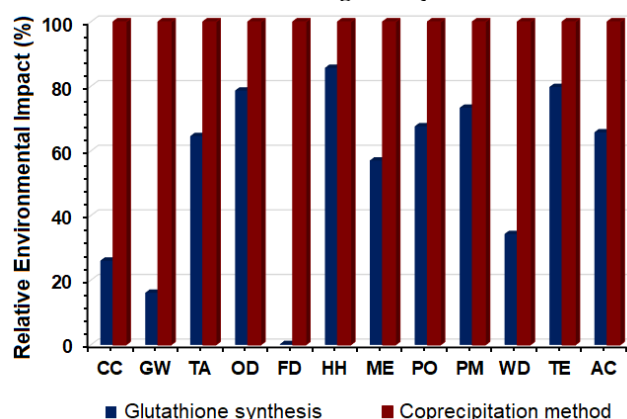


Figure 4. Relative environmental impacts of the Fe₃O₄ nanoparticles synthesis obtained by glutathione and co-precipitation method's (Adapted from Marimón-Bolívar and González (2018)). CC refers to climate change, GW to global warming potential, TA to terrestrial acidification, OD to ozone depletion, FD to fossil depletion, HH to human toxicity, ME to marine eutrophication, PO to photochemical oxidant formation, PM to particular matter formation, WD to water depletion, TE to terrestrial eutrophication, and AC to acidification.²⁵

On the other hand, it is widely accepted that LCA allows contrasting the ecological impacts of a process, evaluating the aspects to be optimized, and comparing different methodologies to obtain analogous compounds. However, it should be taken in consideration that the LCA is a quantitative tool subject to qualitative aspects regarding the definition of the goal and scope, therefore, LCA is not a universal descriptor of environmental impact or sustainability; besides, LCA

presents a notable disadvantage in the evaluation of emerging technologies in terms of limited access to data and differences between them depending on the source of information consulted, and therefore, assumptions or using averages of a general material for a particular process are usually required.^{39,74,93} Thus, the fact that the fate-exposure-effect models are established from the quantities released into the environment, the need to introduce assumptions, the strong limitation of the information available for making comparisons, together with the unavailability of standardized systems for the recording of initial information, and the tendency in the field of nanotechnology to focus on potential applications in a race to develop new technologies, slow down the advance of metrics for the description of the environmental impact of different methods of nanomaterial production, in particular, the adaptation of the LCA and its harmonization with the principles of green chemistry.^{16,32,33,74,88,90,94,95}

However, LCA has been directed to continue advancing and has been implemented within the scientific and productive culture, in such a way that simulation tools focused on the LCA of nanomaterials have been developed. By instance, the simulation tools RedNano and LearNano.⁹⁶ The first one uses the MendNano modelling platform of nanomaterial's environmental concentration based on climatic conditions and size distribution, whereas the second one is focused on the estimating of the release of nanomaterials across the life cycle.⁹⁶ In addition, results evidence that problems to face are much, even in the cases of greater eco-friendly projection, for example, in nanobiotechnology and biobased synthesis, the performing of LCA of raw materials obtained from plants is intricate because the agricultural industry is dependent on geography and

time, decentralized, and related to production techniques; but also, since the ecological impact must be considered not only in terms of the land usage but rather in the application of pesticides, usage of water, and greenhouse gas emissions of NO₂, it is evident that quantitatively establishing the net impact on the ecosystem is complex for processes using plant material for nanomaterial synthesis.^{74,81,97} Thus, available data in most of the investigations do not allow to carry out LCA of the processes to evaluate holistically their sustainability.

GREEN NANOMATERIALS IN SOIL REMEDIATION

Green nanomaterials constitute a promising alternative for the development of efficient, eco-friendly, and sustainable alternatives to eliminate emerging pollutants and mixed contaminants through novel remediation methods. However, green-synthesized nanomaterials are, from a broad view, promissory products from a still-emerging area; they have been mostly evaluated for reducing the pollutant concentration at laboratory scale or in simplified models of natural systems, in consequence, its analysis in field, or in real conditions of use, is still incipient. A wide variety of research have been performed in order to develop and evaluate green nanomaterials as a potential technological solution, and this way, to carry out "green" remediation processes. Thus, one of the most promising alternatives for the development of sustainable, safe, and efficient remediation against a wide range of pollutants in the soil matrix is the use of nanometric iron systems obtained through biobased synthesis, or FeNMs (see Table 3).^{1,14,46,98,99}

Table 3. Green iron-based nanomaterials and their evaluation in environmental remediation.

Nanomaterial	Synthesis	Remarks
Amorphous FeNPs (15 – 100 nm)	Aqueous extract of <i>Ilex paraguariensis</i> leaves, composed primarily of catechins that reduced Fe(III) to nZVI (nano zero-valent iron). ¹⁰⁰	Cr(VI) Oxidation-reduction reactions (up to 100 % in 20 minutes)
Spherical FeNPs (22.6 nm average)	The aqueous extract of the leaves of <i>Embllica officinalis</i> was used for the reduction of Fe(III), at ambient conditions during 10 minutes of stirring. ¹⁰¹	Pb(II) Redox reaction and adsorption (up to 100 ppm in 24 hours)
Spherical FeNPs (70 nm average)	The NPs were synthesized using the aqueous extract of <i>Eucalyptus</i> leaves and FeSO ₄ as a source of Fe, which was carried out at room temperature with an N ₂ atmosphere for 30 minutes. ¹⁰²	Cr(VI) Reduction and adsorption (98.6 % in 8 hours)
Amorphous FeNPs (2 – 120 nm)	The extract of <i>Eucalyptus urophylla</i> , <i>Eucalyptus grandis</i> Leaves, and FeNO ₃ ·9H ₂ O were used to synthesize FeNPs, under ambient temperature, and N ₂ atmosphere, in 8 minutes. ¹⁰³	As(V) Adsorption (55.9 % in 96 hours)
α-Fe ₂ O ₃ NPs (20 – 40 nm)	The culture supernatant of the <i>Bacillus cereus</i> SVK1 bacteria was used for the synthesis of hematite NPs, in alkaline medium with Fe(III), at 37 °C for 48 hours. ¹⁰⁴	Carbamazepine Adsorption (~ 100 % in 150 minutes)
FeOOH NPs (9 – 15 nm)	The exopolysaccharides of the strain <i>Klebsiella oxytoca</i> DSM 29614 were used to synthesize FeOOH NPs	As(III) As(V)

	through the citric fermentation process and the formation of a ferric exopolymeric hydrogel. ¹⁰⁵	Adsorption (87 – 95 % of As(V) in 5 minutes, and 45 – 61 % of As(III) in 5 minutes)
Fe ₂ O ₃ and Fe ₃ O ₄ NPs (10 – 80 nm)	The NPs were obtained by reducing the FeCl ₃ and FeSO ₄ salts with the <i>Parkia speciosa</i> Hassk pod extract under ambient conditions, and subsequent calcination at 400 °C for 2 hours. ¹⁰⁶	Bromophenol blue Photocatalytic degradation (98 % under visible light)
Mesoporous Fe ₃ O ₄ NPs (average pore diameter 7.66 nm)	<i>Peltophorum pterocarpum</i> pod extract and a ferrous sulfate heptahydrate solution were used to obtain NPs in alkaline pH, at 90 °C for 10 minutes. ¹⁰⁷	Methylene Blue Adsorption (89 % in 45 minutes)

NPs: Nanoparticles

Previous statement is based on the fact that FeNMs, due to their nanometric scale, are characterized by a remarkable mobility in soils, being able to interact intimately with the pollutants present in their phases. In addition, in some cases, FeNMs can catalyst photocatalytic reactions and remove pollutants by adsorption and subsequent can be recovered using a magnetic field. Catalytic reactions degrade pollutants through oxidation-reduction in conjunction with Fenton type reactions promoted by nano zero-valent iron (nZVI); whereas, on the other hand, pollutant can be adsorbed on the surface of metallic oxides such as magnetite (Fe₃O₄) and hematite (Fe₂O₃), which are characterized to show magnetic properties.^{23,108-111} Some examples of this strategies are: the investigation carried out by Stan et al. (2017), in which it is analyzed the simultaneous removal by adsorption of emerging pollutant. They observed an efficiency greater than 90 % for removal of pharmaceutical contaminants, specifically, β -lactam-type antibiotics (e.g., piperacillin, tazobactam, ampicillin), polycyclic naphthacene-carboxamide derivatives (tetracycline), and macrolides (erythromycin) in an aqueous solution. They employed magnetite nanoparticles synthesized with agroindustrial wastes (i.e., peel of *Citrus limon*, *Vitis vinifera*, and *Cucumis sativus*).¹¹² In the research carried out by Ramar et al. (2019) was performed the photoreduction of Cr(VI) to Cr(III) and the degradation of the Malachite green dye through the use of hematite nanorods. Nanomaterials were obtained with the stem resin of the *Musa Paradisiaca* Linn, which allowed to carry out the transformation of these pollutants into less dangerous species after 25 minutes of exposure to sunlight.¹¹³ In addition, the concentration of heavy metals such as Pb(II) was reduced to non-detectable levels through an adsorption mechanism and oxidation-reduction processes in a 100 ppm solution of the metal after 24 hours, by adding 20 mL/L of nZVI, which were synthesized from aqueous extracts of the *Emblica officinalis* leaf.¹⁰¹

Compared with other metals, precursors of FeNMs present a greater abundance, lower costs, lower handling risks, greater ease in their operation, and a lower potential risk of ecotoxicity. According with the latter feature, in the case of soils, iron is a micronutrient and

promoter for the growth of phytoremediation plants (e.g., *Lolium perenne*), but also, it is a stimulating of metabolic activity of soil microorganisms; the potential biostimulation capacity of iron is dependent on the concentration, since toxicity processes are generated at concentrations higher than those necessary for the organisms.^{1,23,110,114,115} Therefore, it is expected that the addition of FeNMs to soil, particularly biobased species, does not alter the biogeochemical cycle of iron, since iron hydroxide/oxide nanomaterials can be naturally found at the nanoscale, such as ferrihydrite.¹¹⁶⁻¹²²

It is concluded that, nanoremediation activities based on FeNMs is a potential strategy to favor the removal of pollutants through bioremediation agents, which can be optimized by incorporating biodegradable covering agents and used as a source of nutrients, therefore, FeNMs can be understood as multifunctional hybrid nano-bioremediation agents.^{123,124}

An example of the cost-benefit advantage and compatibility of FeNMs, compared with analogous nanomaterials obtained from noble metals such as silver, can be found in research directed toward the study of degradation efficiency of pollutants by the use of nanobioremediation in aqueous and soil systems, where plants and nanomaterials supported on activated carbon are simultaneously used. In this way, iron nanoparticles synthesized using the aqueous extract of *Ficus sycomorus* leaves and FeCl₃, and silver nanoparticles synthesized using the aqueous extract of *Brassica alba* seeds and AgNO₃ were compared in a same remediation process.¹²⁵ For nanobioremediation, the nanomaterials were separately used, but also, they were used in conjunction with *Plantago major* (which is a land plant species from family *Plantaginaceae*).¹²⁵ Results in aqueous system showed that after 24 hours, the iron nanoparticles allowed the reduction of about 94 % of chlorfenapyr, corresponding to an effectivity higher than 23 % compared with those obtained by individual bioremediation processes, and about 2 % higher compared with the use of silver nanoparticles by the combined system. In the case of the soil system, the silver-based strategy exhibits a 73.0 % remotion capacity, while the iron-based system 71.2 %. Note that, though efficiency obtained between combined systems is not significant, other aspects it should be taken in

consideration like the cost of AgNO_3 respect to the cost of FeCl_3 , the habitual presence of metal in soils, and larger concentrations of iron respect to the presence and concentrations of silver in the environment.

Despite the excellent results evidenced in laboratory-controlled conditions, in the case of *in-situ* remediation, biogeochemical features can significantly influence the remediation capacity of FeNMs because they interact not only with pollutants but also with biotic and abiotic components from soils and groundwater. In addition, depending on the nature of the contamination, its remediation using Fenton-type reactions assisted by nanomaterials may lead to the generation of toxic degradation products and, in consequence, the generation of secondary contamination is a risk that must always be considered and evaluated.^{1,17,23,126,127} In this sense, biobased FeNMs can present a surface with the ability to modulate the interaction between the core and the natural environment. Thus, it has been evidenced that the presence of stabilizing biomaterials with the ability to act as radical scavengers (such as cellulose derivatives, polyphenols, or soil organic matter) delays the oxidation process and decreases the release into the environment of reactive oxygen species (H_2O_2 , $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$), but also, they promote the reducing of the proportion of these substances able to interact with the soil biotic components and organic matter, leading to oxidative stress and degradation, respectively.^{121,122,128-133}

On the other hand, it is important to recognize that biobased FeNMs not only represent an approach to sustainability, since they also constitute a promising alternative for modulating and optimizing the properties of iron nanomaterials. The above is due to conventional FeNMs exhibit a rapid oxidation process and low stability associated with their high surface energy and magnetic attraction, which promotes agglomeration processes and the generation of macrostructures with low mobility in the natural environments.^{114,134} In this context, it has been found that the use of coating and stabilizing agents allows to modulate the agglomeration processes and contribute with a greater assimilation of the FeNM in the environment.¹³³ This statement is based on the fact that bio-based FeNM properties are dependent on both the metallic core and the molecules found on its surface.¹³⁴⁻¹³⁶ By instance, if the covering agent has a negative charge, which alters the point of zero charge of the FeNM, then it is expected that the generation of heteroaggregation processes with microorganisms will be lower due to electrostatic repulsion processes, which avoids unwanted situations such as structural deformation of cells when nanomaterials are embedded in the lipid bilayer.^{101,137-139} Additionally, it has been shown as that the nanomaterial can present relevant characteristics, such as antibacterial activity against plant pathogens, which has been reported in the case of

Fe_2O_3 NPs obtained with *Skimmia laureola* leaf against *Ralstonia solanacearum* and Fe_3O_4 NPs synthesized by *Calotropis procera* against to *Alternaria alternata*.^{140,141} These advantages over conventionally-synthesized FeNMs origin a considerable academic and commercial interest for the use of biobased FeNMs in environmental applications. Therefore, in order to identify and construct a conceptual framework, it is important to analyze the possible interactions of the nanomaterials with natural components of the soil, mainly, those with abiotic nature (i.e., soil atmosphere, soil solution, humified organic matter, and clay minerals).^{142,115}

INTERACTION OF ABIOTIC SOIL COMPONENTS WITH BIOBASED NANOMATERIALS

First, it is expected that the growing technological advances in the area of nanoremediation with biobased FeNMs will lead to an increase in the release of this nanomaterials to the environment. In this sense, the knowledge of the behavior of these materials in natural environments, from the point of view of their interaction with soil components, emerges as a starting point of great relevance. It is clear that these interactions are directly related to the effectiveness of environmental remediation and potential effects of these on the environment.^{137,143}

In the same order of ideas previously exposed, the oxidation behavior of biobased FeNMs has been evaluated in the presence of atmospheric air, which can be interpreted as a first approximation to know the potential effects of the soil gas phase in the chemical behavior of nZVI and iron oxide nanomaterials. Thus, it has been evidenced that the presence of an antioxidant capping agent provides the ability to delay the oxidation process of the FeNM, reducing the effects of molecular oxygen in the shell and core of the structure and acting as a temporary barrier to the oxidative process.^{122,144} In this way, Wang et al. (2014) showed how quasi-spherical shaped nanomaterials were obtained by green tea, and eucalyptus leaves extracts, individually, the use of these tissues allowed the formation of NPs with the presence of a core of Fe^0 , a shell of iron oxides, and a surface composed of polyphenols. It was observed that these antioxidant agents confer a protective layer that allows, after two months of exposing the nanomaterial to air, to show practically the same reactivity against the process of transformation of NO_3^- into NH_4^+ mediated by the oxidation of Fe^0 .¹⁴⁵ The stability of nanomaterials synthesized by means of plant extracts is characterized to show a notorious effect against the oxidative process of nZVI. In the context of stability in the atmosphere, natural coverage with antioxidant agents represents an effective alternative to delay the oxidation process of FeNMs. In general, experiments based on tests of in-air oxidation are a simple approximation to describe

potential interactions among FeNMs and soil atmosphere. This situation also has been evidenced in aqueous solution, for example Yi et al. (2019) carried out an aging analysis of amorphous spherical-shaped nanomaterials constituted by a mixture of Fe⁰, FeO, Fe₂O₃, and Fe₃O₄. They synthesized FeNMs using *Eichhornia crassipes* extracts, with the presence of flavonoids, organic acids, and polyphenols. The nanomaterials synthesized with the fresh extract showed the ability to remove 89.3 % of Cr(VI), which decreased to 70.3 % after an aging process of the nanomaterial in an aqueous medium for 28 days.¹⁴⁶ In contrast, when the extract was aged for 28 days, a lower antioxidant capacity (15.4 %) was evidenced. In addition, this extract was employed to obtain the nanomaterial, and their Cr(VI) removal capacity was 67.2 %, a lower value than the aged nanomaterials of the fresh extract products. Therefore, the relevance of the antioxidant capacity in the conservation of reactivity was observed and directly related to the structure's passivation in an aqueous medium and with surface coating biomolecules.¹⁴⁶ Thus, FeNMs emerge as remedial agents with improved useful life and resistance to oxidation reactions in comparison with conventional FeNMs.

On the other hand, the presence of natural origin molecules is recognized as the most eco-friendly alternatives to avoid the aggregation process, which have been associated with interactions among covering agents and several soil components. In particular, the stabilization of nanoparticles in aqueous systems is mediated by steric and/or electrostatic phenomena.^{137,146,147} Under this approach, more stable FeNMs have been synthesized using starch coatings that provide steric stabilization to the nZVI particles. Particularly, this biomolecule is obtained by a purified way or by extracts of vegetal biomass, such as *Persea americana*, *Solanum tuberosum*, and *Citrullus lanatus*.^{112,148,149} In the case of biobased nanomaterials, it has been shown that functional groups onto coating act as chelating agents for metal cations and favor another type of agglomeration respect to electrostatic interaction.^{150,151} Such is the case of nanomaterials composed of a core of nZVI and a covering of the starch biomolecule, which in the presence of calcium cations carry out complexation processes through hydroxyl groups. In this system, calcium ions act as a bridge between the coatings of the nanomaterials from different particles. Thus, effective size of the particle is increased, and aggregation-sedimentation processes are produced.^{145,150,152} For this reason, biobased FeNMs coated with biomolecules able to complex cations is usually one not very viable alternative to carry out nanoremediation processes in dissolutions with a considerable calcium content (e.g., in limestone-rich soils).¹⁵³

Regarding the interaction between biobased FeNMs and soil organic matter, it is established that in the presence

of humic acid, nanomaterials obtained with this covering agent will not undergo homoaggregation processes at low ionic force.^{152,154,155} On the contrary, if the coating agent of biobased FeNMs can present attractive or stabilizing interactions with humic substances, the humified organic matter can act as a binding agent. Such is the case of the agglomeration processes of nZVI with a surface composed of starch biomolecules, that in the presence of humic acids, act as an aggregation and sedimentation agent by interacting attractively with the capping of two different particles, increasing the effective size of the particle.^{156,145} On the other hand, due to the reactivity of FeNMs in the aging process, they generate Fe(II) cations, oxides, and hydroxides, which in the natural environment can act as catalysts for Fenton-type reactions.^{109,157,158} These reactions are non-selective oxidative processes able of generating organic compound's degradation.^{137,159} Therefore, the presence of an organic component, such as humic substances, is expected to exhibit alterations in their structure by the increase in the proportion of reactive oxygen molecules in the natural environment, which are able to generate the degradation of endogenous organic components, but also, they are able to undergo complexation processes for the generation of Fe-fulvate and Fe-humate.^{137,159,160}

On the other hand, clay's electrostatic characteristics allow them to interact non-selectively with charged substances present in the medium. Such is the case of iron oxides, which present a point of zero charge between 7.2 and 9.5 (7.9 in the case of ferrihydrite, 8.5 for hematite, 9.0 - 9.4 for goethite), this implies that at a pH lower than these values present a positive charge.^{137,161-163} Consequently, in most soils, positive charge iron-based nanoparticles can interact attractively with the clays, generating heteroaggregation processes mediated by adsorption with the consequent alteration of the surface charge of the clay and could altering the microstructure of the natural component by interlaminar intercalation processes.^{6,163} However, these attractive interactions between FeNMs and clays can be modified by altering the nanomaterial's point of zero charge through surface modification processes.¹⁵² This approach has been evidenced in biobased syntheses of iron nanomaterials since the components that allow stabilization of them in homoaggregation processes can be anionic polyelectrolytes, which can favor repulsion interactions between clays and FeNMs.^{105,137,146,148} Evidence of this is the research carried out by Casentini et al. (2019), who used a microbiological approach employing the strain *Klebsiella oxytoca* DSM 29614 to obtain nanomaterials of FeOOH with coverage of exopolysaccharides. They obtained FeNMs with a dimension between 9 and 15 nm and a point of zero charge of 3.2.¹⁰⁵ Therefore, at a higher pH, the material has a negative charge; that is, at conditions of normal pH for the soils, it is expected that this material will present

repulsive interactions with the clay's surface, avoiding heteroaggregation situations.¹⁰⁵ In turn, it has been shown that other biobased approaches using plant biomolecules can also be employed to reduce the point of zero charge of nZVI through the presence of the starch capping agent, with which the point of zero charge for the nZVI corresponds to 3.8, that is, under natural conditions, it is expected that they will not present attractive interactions with clays.¹⁵⁰

The transformations and interactions of nanomaterials with soil components considered in this section in an individually manner co-occur in the natural system, so it is necessary to advance in understand the behavior of biobased FeNMs with the natural system from a holistic and systemic point of view. It is highlighted that the structural and chemical properties of nanomaterials in a natural environment are expected to differ in some proportion from those exposed in laboratory conditions, so progress must be made in the development and implementation of methodologies that allow analyzing and understand the behavior and temporary transformation of FeNMs and biomolecules from most-complex model systems and with different types of soils.

LIMITATIONS AND PROSPECTS OF GREEN NANOMATERIALS IN NANOREMEDIATION

Based on the information presented in the previous sections, it is clear that the use of biobased FeNMs in processes for nanoremediation is a promising technology for sustainable environmental remediation, therefore, this technology represents a field of interest not only for the scientific community but also for government entities that hope, through the implementation of this technology, to tackle the technological problem that involves the remediation of natural systems. In this way, projects such as NanoRem (Nanotechnology for the Remediation of Contaminated Soils) (2013 – 2017) have been developed, which investigated the use of FeNMs for environmental remediation activities in the European Union, and at the same time, it is proposed to advance in the commercialization of nanoproducts, like bionanomagnetite, for the *in-situ* remediation of soils and groundwater, and oriented towards an ecological design.^{164,165} These pilots allowed progress in the development of the structure-activity and risk-benefit relationships of nanoremediations, their market, and LCA.^{164,165} From the perspective of sustainability, the NANOBOND project of POR CReO FESR (2014 – 2020) was focused on establishing a sustainable remediation of sludge and sediment through hybrid technologies, using dewatering tubes and nanostructured materials with adsorption capacity of organic and inorganic pollutants under an environmentally safe guidance and generated from renewable resources.¹⁶⁴ Similarly, the

TANIA project (Pollution Treatment through Nanoremediation) (2017 – 2021) seeks to advance in the development of standardized methodologies, pilot applications, and regulations of nanomaterials in soil and water nanoremediation processes through a sustainable and safe approach.¹⁶⁴ In conclusion, these projects demonstrate the relevance and market potential of synthesized nanomaterials through holistic sustainability considerations in environmental remediation.

However, green nanomaterials for environmental remediation present notable limitations, primarily those associated with intrinsic nature of nanostructures, the inherent molecular variability of biosynthetic agents, and the complexity in the nanomaterial-natural system interactions that hinder their LCA.²⁹ In a slightly more specific way, nanomaterials synthesized through biological molecules or organisms present difficulties in their reproducibility because their molecular composition is not static and dependent on nutritional conditions, stressors, and interactions with the environment.^{66,152} On the other hand, scientific community and governments must advance in the development of international parameters allowing to define standards, protocols, and universal regulations for the evaluation and implementation of nanotechnological materials for environmental applications. Also, it is necessary to advance in the development of nanomaterial libraries to achieve a generalized and available information about surface properties, interactions, and risk of the nanomaterials.^{11,23,41,131,166}

CONCLUSIONS

The continuous release of manufactured residues, products, and by-products represent a constant danger for sustainability of living in the planet. Consequently, mitigation and remediation strategies able to improve or restore the ecosystems without producing a direct or indirect negative impact are strongly desired. Between efficient, fast, and eco-friendly alternatives for environmental remediation processes is the use of nanomaterials, which should be ideally synthesized under the design precepts of green chemistry and environmental sustainability. However, it is evidenced that according as these concepts are qualitative, they are subject to temporal, geographical, commercial, and perceptual conceptions, and therefore, the label “green” is not usually an adequate synonym for sustainability, and even, “green” is frequently used as an analog of nanobiotechnological or bio-based synthesis. The above makes it necessary to apply metrics or minimum criteria to designate a process as green, for that it is not appropriate to define if a synthetic methodology is green without prior analysis of its ecological impacts, due to

the lack of this practice is common employ green as a synonym of biobased. On the other hand, bio-based nanomaterials, primarily those composed by iron, can be applied as active components in remediation systems; where depending on nature, synthesis, composition, morphological features, and usage environment, nanomaterials can interact, reduce, immobilize, and removal a wide variety of pollutants, and the biological surface allows delaying the oxidation and homoagglomeration process characteristic of bare iron-based nanomaterials obtaining by conventional approaches. However, due to that the environmental biobased nanotechnology is an area still emerging, several aspects must be evaluated and carefully analyzed before their application at a commercial level and under real conditions.

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ASSOCIATED PRODUCTS

1. Palencia, M.; García-Quintero, A. Green synthesis of nanomaterials and their use in bio- and nanoremediation. In *Bio- and Nanoremediation of Hazardous Pollutants*. CRC Press, **2021**. (In edition).
2. García-Quintero, A.; Palencia, M. A critical analysis of sustainability metrics applied to green synthesis of nanomaterials and the assessment of environmental risks associated with the nanotechnology. In review by *Sci. Total Environ.* **2021**.
3. García-Quintero, A.; Palencia, M. Interactions among biobased iron nanomaterials and soil abiotic components – A review. *J. Sci. Technol. Appl.* **2021**, 10, 4–26. <https://doi.org/10.34294/j.jsta.20.9.59>

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REFERENCES

1. Cecchin, I.; Reddy, K.R.; Thomé, A.; Tessaro, E.F.; Shnaid, F. Nanobioremediation: integration of nanoparticles and bioremediation for sustainable remediation of chlorinated organic contaminants in soils. *Int. Biodeterior. Biodegrad.* **2017**, 119, 419–428. DOI: 10.1016/j.ibiod.2016.09.027
2. Haider, S.; Haider, A.; Ahmad, A.; Khan, S.U.; Almasry, W.A.; Sarfarz, M. Electrospun nanofibers affinity membranes for water hazards remediation. *Nanotechnol. Res. J.* **2015**, 8 (4), 511–541. DOI: 10.1080/15583724.2017.1309664
3. Livingston, A.; Trout, B.L.; Horvath, I.T.; Johnson, M.D.; Vaccaro, L.; Coronas, J.; Babbitt, C.W.; Zhang, X.; Pradeep, T.; Drioli, E.; Hayler, J.D.; Tam, K.C.; Kappe, O.; Fane, A.G.; Szekely, G. Challenges and directions for green chemical engineering – Role of nanoscale materials. In *Sustainable nanoscale engineering: from materials design to chemical processing*. Elsevier, **2020**; pp 1–18. DOI: 10.1016/B978-0-12-814681-1.00001-1
4. Mehdinia, A.; Mehrabi, H. Application of nanomaterials for removal environmental pollution. In *Industrial applications of nanomaterials*. Elsevier, **2019**; pp 365–402. DOI: 10.1016/B978-0-12-815749-7.00013-X
5. Ashraf, M.A.; Maah, M.J.; Yusoff, I. Soil Contamination, Risk Assessment and Remediation. In *Environmental Risk Assessment of Soil Contamination*. IntechOpen, **2014**. DOI: 10.5772/57287
6. Dror, I.; Yaron, B.; Berkowitz, B. Microchemical contaminants as forming agents of anthropogenic soils. *Ambio.* **2017**, 46, 109–120. DOI: 10.1007/s13280-016-0804-7
7. Kanwar, P.; Mishra, T.; Mukherjee, G. Microbial remediation of hazardous heavy metals. In *Bioremediation and sustainable technologies for cleaner environment*. Springer International Publishing, **2017**; pp 581–293. DOI: 10.1007/978-3-319-48439-6_21
8. Garcés, V.; Lerma, T.A.; Palencia, M.; Combatt, E.M. Building a probe-type passive sampler to study the contents of heavy metals in the aqueous phase in the soil. *J. Sci. Technol. Appl.* **2018**, 4, 4–16. DOI: 10.34294/j.jsta.18.4.26
9. Hasan, M.K.; Shopan, J.; Ahammed, G.J. Nanomaterials and soil health for agricultural crop production: current status and future prospects. In *Nanomaterials for agriculture and forestry applications*. Elsevier, **2020**; pp 289–312. DOI: 10.1016/B978-0-12-817852-2.00012-3
10. Lerma, T.A.; Combatt, E.M.; Palencia, M. Soil-mimicking hybrid composites based on clay, polymers and nitrogen-fixing bacteria for the development of remediation systems of degraded soil. *J. Sci. Technol. Appl.* **2018**, 4, 17–27. DOI: 10.1016/10.34294/j.jsta.18.4.27
11. Sohail, M.I.; Waris, A.A.; Ayub, M.A.; Usman, M.; Rehman, M.Z.; Sabir, M.; Faiz, T. Environmental application of nanomaterials. *Compr. Anal. Chem.* **2019**, 87, 1–54. DOI: 10.1016/bs.coac.2019.10.002
12. Tripathi, C.S.; Sanjeevi, R.; Jayaraman, A.; Singh, D.; Rathoure, A.K. Nano-Bioremediation: Nanotechnology and Bioremediation. In *Biostimulation remediation technologies for groundwater contaminants*. IGI Global, **2018**; pp 202–209. DOI: 10.4018/978-1-5225-4162-2.ch012
13. Qian, Y.; Qin, C.; Chen, M.; Lin, S. Nanotechnology in soil remediation–applications vs. implications. *Ecotox. Environ. Safe.* **2020**, 201, 110815. DOI: 10.1016/j.ecoenv.2020.110815
14. Bandala, E.R.; Berli, M. Nanomaterials: New Agrotechnology Tools to Improve Soil Quality? In *Agricultural Nanobiotechnology*. Springer International Publishing, **2018**; pp 127–140. DOI: 10.1007/978-3-319-96719-6_7
15. Hou, D.; O'Connor, D. Green and sustainable remediation: concepts, principles, and pertaining research. In *Sustainable*

- Remediation of Contaminated Soil and Groundwater*. Elsevier, **2020**; pp 1–17. DOI: 10.1016/B978-0-12-817982-6.00001-X
16. Poynton, H.; Robinson, W.E. Contaminants of emerging concern, with an emphasis on nanomaterials and pharmaceuticals. In *Green chemistry*. Elsevier, **2018**; pp 291–315. DOI: 10.1016/B978-0-12-809270-5.00012-1
 17. Singh, R.; Behera, M.; Kumar, S. Nano-bioremediation: an innovative remediation technology for treatment and management of contaminated sites. In *Bioremediation of industrial waste for environmental safety*. Springer, **2020**; pp 165–182. DOI: 10.1007/978-981-13-3426-9_7
 18. Shah, M.; Fawcett, D.; Sharma, S.; Tripathy, S.K.; Ponern, G.E.J. Green synthesis of metallic nanoparticles via biological entities. *Materials*. **2015**, *8* (11), 7278–7308. DOI: 10.3390/ma8115377
 19. Davies, A.S.; Prakash, P.; Thamaraiselvi, K. Nanobioremediation technologies for sustainable environment. In *Bioremediation and sustainable technologies for cleaner environment*. Springer International Publishing, **2017**; pp 581–293. DOI: 10.1007/978-3-319-48439-6_2
 20. González-Ballesteros, N.; Rodríguez-Argüelles, M.C. Seaweeds: A promising bionanofactory for ecofriendly synthesis of gold and silver nanoparticles. In *Sustainable Seaweed Technologies*. Elsevier, **2020**; pp 507–541. DOI: 10.1016/B978-0-12-817943-7.00018-4
 21. Villalobos, R.J.; Rojas, D.; Díaz, A.; Ramírez, J.; Meléndrez, M.; Flores, P. Synthesis and characterization of 1D metal oxide nano-structures: titanium dioxide nanotubes (TNTs) and zinc oxide nanobars (ZNBs). *J. Sci. Technol. Appl.* **2019**, *6*, 79–95. DOI: 10.34294/j.jsta.19.6.43
 22. Pandey, G. Prospects of Nanobioremediation in Environmental cleanup. *Orient. J. Chem.* **2018**, *34* (6), 2828–2840. DOI: 10.13005/ojc/340622
 23. Iavicoli, I.; Leso, V.; Beezhold, D.H.; Shvedova, A.A. Nanotechnology in agriculture: opportunities, toxicological implications, and occupational risks. *Toxicol. Appl. Pharmacol.* **2017**, *329*, 96–111. DOI: 10.1016/j.taap.2017.05.025
 24. Bolade, O.P.; Williams, A.B.; Benson, N.U. Green synthesis of iron-based nanomaterials for environmental remediation: a review. *Environ. Nanotech. Monit. & Manage.* **2020**, *13*, 100279. DOI: 10.1016/j.enmm.2019.100279
 25. García-Quintero, A.; Palencia, M. A critical analysis of sustainability metrics applied to green synthesis of nanomaterials and the assessment of environmental risks associated with the nanotechnology. *Sci. Total Environ.* **2021**. (In review).
 26. Anastas, N.D. Incentives for using green chemistry and the presentation of an approach for green chemical design. In *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*. John Wiley and Sons Ltd, **2008**; pp 27–40. DOI: 10.1002/9781444305432.ch2
 27. Coish, P.; McGovern, E.; Zimmerman, J.B.; Anastas, P.T. The value-adding connections between the management of ecoinnovation and the principles of green chemistry and green engineering. In *Green chemistry*. Elsevier, **2018**; pp 981–998. DOI: 10.1016/B978-0-12-809270-5.00033-9
 28. Albini, A.; Protti, S. *Paradigms in Green Chemistry and Technology*. Springer International Publishing, **2016**. DOI: 10.1007/978-3-319-25895-9
 29. Khan, S.H. Green nanotechnology for the environment and sustainable development. In *Green materials for wastewater treatment*. Springer International Publishing, **2020**; pp 13–46. DOI: 10.1007/978-3-030-17724-9_2
 30. Eckelman, M.J.; Zimmerman, J.B.; Anastas, P.T. Toward green nano. *J. Ind. Ecol.* **2008**, *12* (3), 316–328. DOI: 10.1111/j.1530-9290.2008.00043.x
 31. Dahl, J.A.; Maddux, B.L.S.; Hutchinson, J.E. Toward greener nanosynthesis. *Chem. Rev.* **2007**, *107*, 2228–2269. DOI: 10.1021/cr050943k
 32. Gilbertson, L.M.; Zimmerman, J.B.; Plata, D.L.; Hutchison, J.E.; Anastas, P.T. Designing nanomaterials to maximize performance and minimize undesirable implications guided by the principles of green chemistry. *Chem. Soc. Rev.* **2015**, *44*, 5758–5777. DOI: 10.1039/c4cs00445k
 33. Ciambelli, P.; La Guardia, G.; Vitale, L. Nanotechnology for green materials and processes. In *Catalysis, green chemistry and sustainable energy*. Elsevier, **2019**; pp 97–116. DOI: 10.1016/B978-0-444-64337-7.00007-0
 34. Dicks, A.P.; Hent, A. *Green chemistry metrics*. Springer International Publishing., **2015**. DOI: 10.1007/978-3-319-10500-0
 35. Silva, L.P.; Garcez, I.; Bonatto, C.C. Green synthesis of metal nanoparticles by plants. In *Green processes for nanotechnology*. Springer International Publishing, **2015**; pp 259–275. DOI: 10.1007/978-3-319-15461-9_9
 36. Mulvihill, M.J.; Beach, E.S.; Zimmerman, J.B.; Anastas, P.T. Green chemistry and green engineering: a framework for sustainable technology development. *Annu. Rev.* **2011**, *36*, 271–293. DOI: 10.1146/annurev-environ-032009-095500
 37. Palencia, M.; Córdoba, A.; Rivas, B.L. Concentration–polarization effect of poly(sodium styrene sulfonate) on size distribution of colloidal silver nanoparticles during diafiltration experiments. *Colloid. Polym. Sci.* **2014**, *292*, 619–626. DOI: 10.1007/s00396-013-3096-5
 38. Palencia, M.; Rivas, B.L.; Valle, H. Size separation of silver nanoparticles by dead-end ultrafiltration: Description of fouling mechanism by pore blocking model. *J. Membr. Sci.* **2014**, *455*, 7–14. DOI: 10.1016/j.memsci.2013.12.051
 39. Anastas, N.D.; Leazer, J.; Gonzalez, M.A.; DeVito, S.C. Expanding rational molecular design beyond pharma. In *Handbook of green chemistry, volume 11: Green metrics*. Wiley BCH, **2018**; pp 29–48. DOI: 10.1002/9783527628698.hgc125
 40. Harper, S.L.; Dahl, J.A.; Maddux, B.L.S.; Tanguay, R.L.; Hutchison J.E. Proactively designing nanomaterials to enhance performance and minimize hazard. *Int. J. Nanotechnol.* **2008**, *5*, 124. DOI: 10.1504/ijnt.2008.016552
 41. Li, Y.; Wang, J.; Zhao, F.; Bai, B.; Nie, G.; Nel, A.E.; Zhao, Y. Nanomaterial libraries and model organisms for rapid high-content analysis of nanosafety. *Natl. Sci. Rev.* **2018**, *5*, 365–388. DOI: 10.1093/nsr/nwx120

42. Khan, S.A.; Lee, C. Green biological synthesis of nanoparticles and their biomedical applications. In *Green processes for nanotechnology*. Springer International Publishing, **2015**; pp 207–235. DOI: 10.1007/978-3-030-4
43. Upreti, G.; Dhingra, R.; Naidu, S.; Atuahene, I.; Sawhney, R. Life Cycle Assessment of nanomaterials. In *Green processes for nanotechnology*. Springer International Publishing, **2015**; pp 393–408. DOI: 10.1007/978-3-319-15461-9_14
44. Erythropel, H.C.; Zimmerman, J.B.; de Winter, T.M.; Petitjean, L.; Melnikov, F.; Lam, C.H.; Lounsbury, A.; Mellor, K.; Jankovića, N.; Tu, Q.; Pincus, L.; Falinski, M.; Shi, W.; Coish, P.; Plata, D.; Anastas, P.T. The Green ChemisTREE: 20 years after taking root with the 12 principles. *Green. Chem.* **2018**, *20*, 1929–1961. DOI: 10.1039/c8gc00482j
45. Sanjay, S.S. Safe nano is green nano. In *Green synthesis, characterization and applications of nanoparticles*. Elsevier, **2019**; pp 27–36. DOI: 10.1016/B978-0-08-102579-6.00002-2
46. Bhandari, G. Environmental Nanotechnology: Applications of Nanoparticles for Bioremediation. In *Approaches in Bioremediation: The new era of environmental microbiology and nanobiotechnology*. Springer International Publishing, **2018**; pp 301–315. DOI: 10.1007/978-3-030-02369-0_13
47. Córdoba, A.; Palencia, M. Development of nanostructured crosslinkers with antimicrobial properties for free-radical polymerization. *J. Sci. Technol. Appl.* **2017**, *2*, 54–64. DOI: 10.34294/j.jsta.17.2.14
48. Kolahalam, L.A.; Kasi, I.V.; Diwakar, B.S.; Govindh, B.; Reddy, V.; Murthy, Y.L.N. Review on nanomaterials. *Mater. Today: Proc.* **2019**, *18*, 2182–2190. DOI: 10.1016/j.matpr.2019.07.371
49. Mohammadi, P.; Hesari, M.; Samadian, H.; Hajialyani, M.; Bayrami, Z.; Farzaei, M.H.; Abdollahi, M. Recent advancements and new perspective of phytonanotechnology. In *Analysis, fate, and toxicity of engineered nanomaterials in plants*. Elsevier, **2019**; pp 1–22. DOI: 10.1016/bs.coac.2019.04.011
50. Anastas, P.T.; Lankey, R.L. Life cycle assessment and green chemistry: the yin and yang of industrial ecology. *Green. Chem.* **2000**, *2*, 289–295. DOI: 10.1039/b005650m
51. Nasrollahzadeh, M.; Atarod, M.; Sajjadi, M.; Sajadi, S.M.; Issaabadi, Z. Plant-mediated green synthesis of nanostructures. In *An Introduction to Green Nanotechnology*. Elsevier, **2015**; pp 199–322. DOI: 10.1016/B978-0-12-813586-0.00006-7
52. Devatha, C.P.; Thala, A.K. Green Synthesis of Nanomaterials. In *Synthesis of Inorganic Nanomaterials*. Elsevier, **2018**; pp 169–148. DOI: 10.1016/B978-0-08-101975-7.00007-5
53. Sebastian, A.; Nangia, A.; Majeti, P. Advances in agrochemical remediation using nanoparticles. In *Agrochemicals: detection, treatment and remediation*. Butterworth-Heinemann, **2020**; pp 465–485. DOI: 10.1016/B978-0-08-103017-2.00018-0
54. Palencia, M.; García-Quintero, A. Green synthesis of nanomaterials and their use in bio- and nanoremediation. In *Bio- and Nanoremediation of Hazardous Pollutants*. CRC Press, **2021**. In edition.
55. Karpagavinayagam, P.; Vedhi, C. Green synthesis of iron oxide nanoparticles using *Avicennia marina* flower extract. *Vacuum.* **2018**, *160*, 286–292. DOI: 10.1016/j.vacuum.2018.11.043
56. Chand, K.; Jiao, C.; Lakhan, M.N.; Shah, A.H.; Kumar, V.; Fouad, D.E.; Chandio, M.B.; Maitlo, A.A.; Ahmed, M.; Cao, D. Green synthesis, characterization and photocatalytic activity of silver nanoparticles synthesized with *Nigella Sativa* seed extract. *Chem. Phys. Lett.* **2021**, *763*, 138218. DOI: 10.1016/j.cplett.2020.138218
57. Nasiri, J.; Rahimi, M.; Hamezadeh, Z.; Motamedi, E.; Naghavi, M.R. Fulfillment of green chemistry for synthesis of silver nanoparticles using root and leaf extracts of *Ferula persica*: Solid-state route vs. solution-phase method. *J. Clean. Prod.* **2018**, *192*, 514–530. DOI: 10.1016/j.jclepro.2018.04.218
58. Santhosh, A.; Theertha, V.; Prakash, P.; Chandran, S. From waste to a value added product: Green synthesis of silver nanoparticles from onion peels together with its diverse applications. *Mat. Today: Proceedings.* **2020**, In press. DOI: 10.1016/j.matpr.2020.09.680
59. Shabaani, M.; Rahaiee, S.; Zare, M.; Jafari, S.M. Green synthesis of ZnO nanoparticles using loquat seed extract; biological functions and photocatalytic degradation properties. *LWT*, **2020**, 110133. DOI: 10.1016/j.lwt.2020.110133
60. Akhlaghi, N.; Najafpour-Darzi, G.; Younesi, H. Facile and green synthesis of cobalt oxide nanoparticles using ethanolic extract of *Trigonella foenum-graceum* (Fenugreek) leaves. *Adv. Powder Technol.* **2020**, *31*, 3562–3569. DOI: 10.1016/j.apt.2020.07.004
61. Abbas, S.; Nasreen, S.; Haroon, A.; Ashraf, M.A. Synthesis of silver and copper nanoparticles from plants and application as adsorbents for naphthalene decontamination. *Saudi J. Biol. Sci.* **2020**, *27*, 1016–1023. DOI: 10.1016/j.sjbs.2020.02.011
62. Liu, H.; Ren, M.; Qu, J.; Feng, Y.; Song, X.; Zhang, Q.; Cong, Q.; Yuan, X. A cost-effective method for recycling carbon and metals in plants: synthesizing nanomaterials. *Environ. Sci. nano.* **2017**, *4*, 461–469. DOI: 10.1039/C6EN00287K
63. Sharma, J.K.; Srivastava, P.; Ameen, S.; Akhtar, M.S.; Sengupta, S.K.; Singh, G. Phytoconstituents assisted green synthesis of cerium oxide nanoparticles for thermal decomposition and dye remediation. *Mater. Res. Bull.* **2017**, *91*, 98–107. DOI: 10.1016/j.materresbull.2017.03.034
64. Nagajyothi, P.C.; Tvm, S. Green synthesis of metallic and metal oxide nanoparticles and their antibacterial activities. In *Green processes for nanotechnology*. Springer International Publishing, **2015**; pp 99–117. DOI: 10.1007/978-3-319-15461-9_4
65. Razavi, M.; Salahinejad, E.; Fahmy, M.; Yazdimamaghani, M.; Vashae, D.; Tayebi, L. Green chemical and biological synthesis of nanoparticles and their biomedical applications. In *Green processes for nanotechnology*. Springer International Publishing, **2015**; pp 207–235. DOI: 10.1007/978-3-319-15461-9_7
66. Srivastava, S.K.; Ogino, C.; Kondo, A. Nanoparticle synthesis by biogenic approach. In *Green Processes for Nanotechnology*. Springer International Publishing, **2015**; pp 237–257. DOI: 10.1007/978-3-319-15461-9_8

67. López-Valdez, F.; Miranda-Arámbula, M.; Ríos-Cortés, A.M.; Fernández-Luqueño, F.; de-la-Luz, V. Nanofertilizers and their controlled delivery of nutrients. In *Agricultural Nanobiotechnology*. Springer International Publishing, **2018**; pp 35–48. DOI: 10.1007/978-3-319-96719-6_
68. Kolahalam, L.A.; Kasi, I.V.; Diwakar, B.S.; Govindh, B.; Reddy, V.; Murthy, Y.L.N. Review on nanomaterials. *Mater. Today: Proc.* **2019**, *18*, 2182–2190. DOI: 10.1016/j.matpr.2019.07.371
69. Wacławek, S.; Gončuková, Z.; Adach, K.; Fijałkowski, M.; Černík, M. Green synthesis of gold nanoparticles using *Artemisia dracunculus* extract. *Environ. Sci. Pollut. Res.* **2018**, *25* (24), 24210–24219. DOI: 10.1007/s11356-018-2510-4
70. Pati, P.; McGinnis, S.; Vikesland, P.J. Life Cycle Assessment of “green” nanoparticle synthesis methods. *Environ. Eng. Sci.* **2014**, *31*, 410–420. DOI: 10.1089/ees.2013.0444
71. Gilbertson, L.M.; Zimmerman, J.B.; Plata, D.L.; Hutchison, J.E.; Anastas, P.T. Designing nanomaterials to maximize performance and minimize undesirable implications guided by the principles of green chemistry. *Chem. Soc. Rev.* **2015**, *44*, 5758–5777. DOI: 10.1039/c4cs00445k
72. Singh, N.; Khan, S. Nanobioremediation: An Innovative Approach to Fluoride (F⁻) Contamination. In *Approaches in Bioremediation: The New Era of environmental microbiology and nanobiotechnology*. Springer International Publishing, **2018**; pp 343–353. DOI: 10.1007/978-3-030-02369-0_15
73. Morales, M.L.; Martínez, J.O.; Reyes-Sánchez, L.B.; Martín, O.; Arroyo, G.A.; Obaya, A.; Miranda, R. How green an experiment is? *Educación Química*. **2011**, *22*, 240–248. DOI: 10.1016/S0187-893X(18)30140-X
74. Tufvesson, L.M.; Tufvesson, P.; Woodley, J.M.; Börjesson, P. Life Cycle Assessment in green chemistry: overview of key parameters and methodological concerns. *Int. J. LCA*. **2012**, *18*, 431–444. DOI: 10.1007/s11367-012-0500-1
75. Tickner, J.A.; Becker, M. Mainstreaming green chemistry: The need for metrics. *Curr. Opin. Green. Sustain. Chem.* **2016**, *1*, 1–4. DOI: 10.1016/j.cogsc.2016.07.002
76. Constable, D.J.C. Green chemistry metrics. In *Handbook of green chemistry, volume 11: Green metrics*. Wiley BCH, **2018**; pp 1–27. DOI: 10.1002/9783527628698.hgc124
77. Muñoz, I. LCA in Green Chemistry: a new subject area and call for papers. *Int. J. LCA*. **2012**, *17*, 517–519. DOI: 10.1007/s11367-012-0410-2
78. Reid, B.T.; Reed, S.M. Improved methods for evaluating the environmental impact of nanoparticle synthesis. *Green Chem.* **2016**, *18* (15), 4263–4269. DOI: 10.1039/c6gc00383d
79. Sheldon, R.A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. *ACS Sust. Chem. Eng.* **2017**, *6* (1), 32–48. DOI: 10.1021/acssuschemeng.7b03505
80. Constable, D.J.C.; Jiménez-Gonzalez, C.; Lapkin, A. Process Metrics. In *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*. John Wiley and Sons Ltd, **2008**; pp 228–257. DOI: 10.1002/9781444305432.ch6
81. DeVierno, A.; House-Knight, T.; Whitford, J.; Ponnusamy, E.; Miller, P.; Jesse, N.; Rodenborn, R.; Sayag, S.; Gebel, M.; Aped, I.; Sharfstein, I.; Manaster, E.; Ergaz, I.; Harris, A.; Nelowet Grice, L. A method for assessing greener alternatives between chemical products following the 12 principles of green chemistry. *ACS Sustain. Chem. Eng.* **2017**, *5* (4), 2927–2935. DOI: 10.1021/acssuschemeng.6b02399
82. Sheldon, R.A. The E factor 25 years on: the rise of green chemistry and sustainability. *Green. Chem.* **2017**, *19* (1), 18–43. DOI: 10.1039/c6gc02157c
83. Goulas, A.; van Ommen, J.R. Scalable production of nanostructured particles using atomic layer deposition. *KONA Powder Part. J.* **2014**, *31* (0), 234–246. DOI: 10.14356/kona.2014013
84. Maity, A.; Polshettiwar, V. Scalable and sustainable synthesis of size-controlled monodisperse dendritic fibrous nanosilica quantified by E-Factor. *ACS Appl. Nano. Mater.* **2018**, *1* (7), 3636–3643. DOI: 10.1021/acsnm.8b00761
85. Meyer, D.E.; Upadhyayula, V.K.K. The use of life cycle tools to support decision making for sustainable nanotechnologies. *Clean Technol. Environ. Policy.* **2013**, *16* (4), 757–772. DOI: 10.1007/s10098-013-0686-3
86. Jiménez-González, C. Life Cycle Assessment. In *Handbook of green chemistry, volume 11: Green metrics*. Wiley BCH, **2018**; pp 95–124. DOI: 10.1002/9783527628698.hgc127
87. Jindal, D.; Jain, I. Role of companies in environmental management through corporate social responsibility and sustainability policy. In *Green chemistry in environmental sustainability and chemical education*. Springer, **2018**; pp 23–42. DOI: 10.1007/978-981-10-8390-7_3
88. Bartolozzi, I.; Daddi, T.; Punta, C.; Fiorati, A.; Iraldo, F. Life cycle assessment of emerging environmental technologies in the early stage of development. *J. Ind. Ecol.* **2019**, *24* (1), 101–115. DOI: 10.1111/jiec.12959
89. Seager, T.P.; Linkov, I. Uncertainty in Life Cycle Assessment of Nanomaterials. In *Nanomaterials: Risks and Benefits. NATO Science for Peace and Security Series C: Environmental Security*. Springer, **2009**; pp 423–436. DOI: 10.1007/978-1-4020-9491-0_33
90. Mortimer, M.; Holden, P.A. Fate of engineered nanomaterials in natural environments and impacts on ecosystems. In *Exposure to Engineered Nanomaterials in the Environment*. William Andrew Publishing, **2019**; pp 61–103. DOI: 10.1016/b978-0-12-814835-8.00003-0
91. Pourzahedi, L.; Eckelman, M.J. Comparative life cycle assessment of silver nanoparticle synthesis routes. *Environ. Sci: nano.* **2015**, *2*, 361–369. DOI: 10.1039/c5en00075k
92. Marimón-Bolívar, W.; González, E.E. Green synthesis with enhanced magnetization and life cycle assessment of Fe₃O₄ nanoparticles. *Environ. Nanotechnol. Monit. Manag.* **2018**, *9*, 58–66. DOI: 10.1016/j.enmm.2017.12.003
93. Romero-Franco, M.; Godwin, H.A.; Bilal, M.; Cohen, Y. Needs and challenges for assessing the environmental impacts of engineered nanomaterials (ENMs). *Beilstein J. Nanotechnol.* **2017**, *8*, 989–1014. DOI: 10.3762/bjnano.8.101

94. Olsen, S.; Jørgensen, M.S. Environmental Assessment of Micro/Nano Production in a Life Cycle Perspective. *MRS Proceedings*. **2005**, 895. DOI: 10.1557/proc-0895-g01-04-s01-04
95. Dhingra, R.; Naidu, S.; Upreti, G.; Sawhney, R. Sustainable Nanotechnology: Through Green Methods and Life-Cycle Thinking. *Sustainability*. **2010**, 2 (10), 3323–3338. DOI: 10.3390/su2103323
96. Gallagher, M.J.; Allen, C.; Buchman, J.T.; Qiu, T.A.; Clement, P.L.; Krause, M.O.P.; Gilbertson, L.M. Research highlights: applications of life-cycle assessment as a tool for characterizing environmental impacts of engineered nanomaterials. *Environ. Sci. Nano*. **2017**, 4 (2), 276–281. DOI: 10.1039/c7en90005h
97. Seager, T.P.; Trump, B.D.; Poinsett-Jones, K.; Linkov, I. Why Life Cycle Assessment Does Not Work for Synthetic Biology. *Environ. Sci. Tech.* **2017**, 51 (11), 5861–5862. DOI: 10.1021/acs.est.7b01604
98. Fajardo, C.; Martín, M.; Nande, M.; Botías, P.; García-Cantalejo, J.; Mengs, G.; Costa, G. Ecotoxicogenomic analysis of stress induce on *Carnorhabditis elegans* in heavy metal contaminated soil after nZVI treatment. *Chemosphere*. **2020**, 254, 126909. DOI: 10.1016/j.chemosphere.2020.126909
99. Ortega-Calvo, J.J.; Jimenez-Sanchez, C.; Pratarolo, P.; Pullin, H.; Scott, T.B.; Thompson, I.P. Tactic response of bacteria to zero-valent iron nanoparticles. *Environ. Pollut.* **2016**, 213, 438–445. DOI: 10.1016/j.envpol.2016.01.093
100. García, F.E.; Senn, A.M.; Meichtry, J.M.; Scott, T.B.; Pullin, H.; Leyva, A.G.; Halac, E.B.; Ramos, C.P.; Sacanell, J.; Mizrahi, M.; Requejo, F.G.; Litter, M.I. Iron-based nanoparticles prepared from yerba mate extract: synthesis, characterization and use on chromium removal. *J. Environ. Manage.* **2019**, 235, 1–8. DOI: 10.1016/j.jenvman.2019.01.002
101. Kumar, R.; Singh, N.; Pandey, S.N. Potential of green synthesized zero-valent iron nanoparticles for remediation of lead-contaminated water. *Int. J. Environ. Sci. Technol.* **2015**, 12, 3943–3950. DOI: 10.1007/s13762-015-0751-z
102. Jin, X.; Liu, Y.; Tan, J.; Owens, G.; Chen, Z. Removal of Cr(VI) from aqueous solutions via reduction and absorption by green synthesized iron nanoparticles. *J. Clean. Prod.* **2018**, 176, 929–936. DOI: 10.1016/j.jclepro.2017.12.026
103. Wu, Z.; Su, X.; Lin, Z.; Owens, G.; Chen, Z. Mechanism of As(V) removal by green synthesized iron nanoparticles. *J. Hazardous Mater.* **2019**, 379, 120811. DOI: 10.1016/j.jhazmat.2019.120811
104. Rajendran, K.; Sen, S. Optimization of process parameters for the rapid biosynthesis of hematite nanoparticles. *J. Photochem. Photobiol. B*. **2016**, 159, 82–87. DOI: 10.1016/j.jphotobiol.2016.03.023
105. Casentini, B.; Gallo, M.; Baldi, F. Arsenate and arsenite removal from contaminated water by iron oxides nanoparticles formed inside a bacterial exopolysaccharide. *J. Environ. Chem. Eng.* **2019**, 7, 102908. DOI: 10.1016/j.jece.2019.102908
106. Fatimah, I.; Pratiwi, E.Z.; Wicaksono, W.P. Synthesis of magnetic nanoparticles using *Parkia speciosa* hassk pod extract and photocatalytic activity for bromophenol blue degradation. *Egypt. J. Aquat. Res.* **2020**, 46, 35–40. DOI: 10.1016/j.ejar.2020.01.001
107. Dash, A.; Ahmed, M.T.; Selvaraj, R. Mesoporous magnetite nanoparticles synthesis using the *Peltophorum pterocarpum* pod extract, their antibacterial efficacy against pathogens and ability to remove a pollutant dye. *J. Mol. Struct.* **2019**, 1178, 268–273. DOI: 10.1016/j.molstruc.2018.10.042
108. Borji, H.; Ayoub, G.M.; Bilbeisi, R.; Nassar, N.; Malaeb, L. How effective are nanomaterials for the removal of heavy metals from water and wastewater? *Water Air Soil. Pollut.* **2020**, 231 (7), 330. DOI: 10.1007/s11270-020-04681-0
109. Galdames, A.; Ruiz-Rubio, L.; Orueta, M.; Sánchez-Arzalluz, M.; Vilas-Vilela, J.L. Zero-valent iron nanoparticles for soil and groundwater remediation. *Int. J. Environ. Res. Public Health*. **2020**, 17 (16), 5817. DOI: 10.3390/ijerph17165817
110. Lu, H.; Wang, J.; Stoller, M.; Wang, T.; Bao, Y.; Hao, H. An overview of nanomaterials for water and wastewater treatment. *Adv. Mater. Sci. Eng.* **2016**, 4964828. DOI: 10.1155/2016/4964828
111. Nour, E.; Hussein, N.N. Biosynthesized magnetite nanoparticles as an environmental opulence and sustainable wastewater treatment. *Sci. Total Environ.* **2021**, 774, 143610. DOI: 10.1016/j.scitotenv.2021.145610
112. Stan, M.; Lung, I.; Soran, M.L.; Leostean, C.; Popa, A.; Stefan, M.; Lazar, M.D.; Opris, O.; Silipas, T.D.; Porav, A.S. Removal of antibiotics from aqueous solutions by green synthesized magnetite nanoparticles with selected agro-waste extracts. *Process. Saf. Environ. Prot.* **2017**, 107, 357–372. DOI: 10.1016/j.psep.2017.03.003
113. Ramar, K.; Ahamed, A.J.; Muralidharan, K. Robust green synthetic approach for the production of iron oxide nanorods and its potential environmental and cytotoxicity applications. *Adv. Powder. Technol.* **2019**, 30 (11), 2636–2648. DOI: 10.1016/j.apt.2019.08.011
114. Mu, Y.; Jia, F.; Ai, Z.; Zhang, L. Iron oxide shell mediated environmental remediation properties of nano zero-valent iron. *Environ. Sci. nano*. **2017**, 4, 27–45. DOI: 10.1039/C6EN00398B
115. Zelić, E.; Vuković, Ž.; Halkijević, I. Application of nanotechnology in wastewater treatment. *Građevinar*. **2018**, 4. DOI: 10.14256/JCE.2165.2017
116. Braunschweig, J.; Bosch, J.; Meckenstock, R.U. Iron oxide nanoparticles in geomicrobiology: from biogeochemistry to bioremediation. *New Biotechnology*. **2013**, 30 (6), 793–802. DOI: 10.1016/j.nbt.2013.03.008
117. Colombo, C.; Iorio, E.; Liu, Q.; Jiang, Z.; Barrón, V. Iron Oxide Nanoparticles in Soils: Environmental and Agronomic Importance. *J. Nanosci. Nanotechnol.* **2017**, 17 (7), 4449–4460. DOI: 10.1166/jnn.2017.14197
118. Figueiredo, M.O.; Silva, T.P.; Veiga, J.P. Natural nanomaterials: reappraising the elusive structure of the nano-sized mineral Ferrihydrite through X-Ray absorption spectroscopy at the iron K-Edge. *Mater. Sci. Forum*. **2012**, 730–732, 931–935. DOI: 10.4028/www.scientific.net/msf.730-732.931

119. Lagroix, F.; Banerjee, S.K.; Jackson, M.J. Geological occurrences and relevance of iron oxides. In *Iron Oxides*. Wiley, **2016**; pp 7–30. DOI: 10.1002/9783527691395.ch2
120. Singh, S.; Husen, A. Behavior of agricultural crops in relation to nanomaterials under adverse environmental conditions. In *Nanomaterials for Agriculture and Forestry Applications*. Elsevier, **2020**; pp 219–256. DOI: 10.1016/b978-0-12-817852-2.00009-3
121. Lefevre, E.; Bossa, N.; Wiesner, M.R.; Gunsch, C.K. A review of the environmental implications of *in situ* remediation by nanoscale zero valent iron (nZVI): Behavior, transport and impacts on microbial communities. *Sci. Total Environ.* **2016**, 565, 889–901. DOI: 10.1016/j.scitotenv.2016.02.003
122. Machado, S.; Pacheco, J.G.; Nouws, H.P.A.; Albergaria, J.T.; Delerue-Matos, C. Characterization of green zero-valent iron nanoparticles produced with tree leaf extracts. *Sci. Total Environ.* **2015**, 533, 76–81. DOI: 10.1016/j.scitotenv.2015.06.091
123. Sasidharan, S.; Raj, S.; Sonawane, S.; Sonawane, S.; Pinjari, D.; Pandit, A.B.; Saudagar, P. Nanomaterial synthesis: chemical and biological route and applications. In *Nanomaterials synthesis: design, fabrication and applications*. Elsevier, **2019**; pp 27–51. DOI: 10.1016/B978-0-12-815751-0.00002-X
124. Vázquez-Núñez, E.; Molina-Guerrero, C.E.; Peña-Castro, J.M.; Fernández-Luqueño, F.; de la Rosa-Álvarez, M.G. Use of nanotechnology for the bioremediation of contaminants: A review. *Processes*. **2020**, 8 (7), 826. DOI: 10.3390/pr8070826
125. Romeh, A.A.; Saber, R.A.I. Green nano-phytoremediation and solubility improving agents for the remediation of chlorfenapyr contaminated soil and water. *J. Environ. Manage.* **2020**, 260, 110104. DOI: 10.1016/j.jenvman.2020.110104
126. Koduru, J.R.; Shankar, S.; More, N.S.; Shikha; Lingamdinne, L.P.; Singh, J. Toxic metals contamination in the environment. In *Environmental pollutants and their bioremediation approaches*. CRC Press, **2017**; pp 209–240. DOI: 10.1201/9781315173351-8
127. Zhang, T.; Lowry, G.V.; Capiro, N.L.; Chen, J.; Chen, W.; Chen, Y.; Dionysiou, D.D.; Elliott, D.W.; Ghoshal, S.; Hofmann, T.; Hsu-Kim, H.; Hughes, J.; Jiang, C.; Jiang, G.; Jing, C.; Kavanaugh, M.; Li, Q.; Liu, S.; Ma, J.; Pan, B.; Phenrat, T.; Qu, X.; Quan, X.; Saleh, N.; Vikesland, P.J.; Wang, Q.; Westerhoff, P.; Wong, M.S.; Xia, T.; Xing, B.; Yan, B.; Zhang, L.; Zhou, D.; Alvarez, P.J.J. *In situ* remediation of subsurface contamination. *Environ. Sci. nano.* **2019**, 6, 1283–1302. DOI: 10.1039/C9EN00143C
128. Carlos, L.; Cipollone, M.; Soria, D.B.; Moreno, M.; Ogilby, P.R.; García Einschlag, F.S.; Mártire, D.O. The effect of humic acid binding to magnetite nanoparticles on the photogeneration of reactive oxygen species. *Sep. Purif. Technol.* **2012**, 91, 23–29. DOI: 10.1016/j.seppur.2011.08.028
129. Chen, J.; Xiu, Z.; Lowry, G.V.; Alvarez, P.J.J. Effect of natural organic matter on toxicity and reactivity of nano-scale zero-valent iron. *Water Res.* **2011**, 45 (5), 1995–2001. DOI: 10.1016/j.watres.2010.11.036
130. Huang, Y.W.; Cambre, M.; Lee, H.J. The toxicity of nanoparticles depends on multiple molecular and physicochemical mechanisms. *Int. J. Mol. Sci.* **2017**, 18 (12), 2702. DOI: 10.3390/ijms18122702
131. Palencia, S.L.; Medina, A.; Palencia, M. Interaction mechanisms of inorganic nanoparticles and biomolecular systems of microorganisms. *Curr. Chem. Biol.* **2015**, 9, 10–22. DOI: 10.2174/2212796809666151022201811
132. Wang, Z.; Fang, C.; Mallavarapu, M. Characterization of iron-polyphenol complex nanoparticles synthesized by Sage (*Salvia officinalis*) leaves. *Environ. Technol. Innov.* **2015**, 4, 92–97. DOI: 10.1016/j.eti.2015.05.004
133. Xie, Y.; Dong, H.; Zeng, G.; Tang, L.; Jiang, Z.; Zhang, C.; Deng, J.; Zhang, L.; Zhang, Y. The interactions between nanoscale zero-valent iron and microbes in the subsurface environment: A review. *J. Hazard Mater.* **2017**, 321, 390–407. DOI: 10.1016/j.jhazmat.2016.09.028
134. Christian, P.; Von der Kammer, F.; Baalousha, M.; Hofmann, T. Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology*. **2008**, 17 (5), 326–343. DOI: 10.1007/s10646-008-0213-1
135. Palencia, M.; Berrio, M.; Melendrez, M. Nanostructured polymer composites with potential applications into the storage of blood and hemoderivates. *J. Sci. Technol. Appl.* **2016**, 1, 4–14. DOI: 10.34294/j.jsta.16.1.1
136. Palencia, M.; Berrio, M.E.; Palencia, S.L. Effect of capping agent and diffusivity of different silver nanoparticles on their antibacterial properties. *J. Nanosci. Nanotechnol.* **2017**, 17, 5197–5204. DOI: 10.1166/jnn.2017.13850
137. Lei, C.; Sun, Y.; Tsang, D.C.W.; Lin, D. Environmental transformations and ecological effects of iron-based nanoparticles. *Environ. Pollut.* **2018**, 232, 10–30. DOI: 10.1016/j.envpol.2017.09.052
138. Palencia, S.L.; Combatt, E.M.; Palencia, M. Toxicity of inorganic nanoparticles in soil microorganism with agricultural importance. A Review. *Temas Agrarios*. **2013**, 108 (2), 106–122. DOI: 10.21897/rta.v18i2.720
139. Palencia, S.L.; Medina, A.; Palencia, M. Interaction mechanisms of inorganic nanoparticles and biomolecular systems of microorganisms. *Curr. Chem. Biol.* **2015**, 9, 10–22. DOI: 10.2174/2212796809666151022201811
140. Alam, T.; Khan, R.A.A.; Ali, A.; Sher, H.; Ullah, Z.; Ali, M. Biogenic synthesis of iron oxide nanoparticles via *Skimmia laureola* and their antibacterial efficacy against bacterial wilt pathogen *Ralstonia solanacearum*. *Mater. Sci. Eng. C*. **2018**, 91, 101–108. DOI: 10.1016/j.msec.2018.12.117
141. Ali, M.; Haroon, U.; Khizar, M.; Chaudhary, H.J.; Hussain Munis, M.F. Facile single step preparations of phyto-nanoparticles of iron in *Calotropis procera* leaf extract to evaluate their antifungal potential against *Alternaria alternata*. *Curr. Plant. Biol.* **2020**, 23, 100157. DOI: 10.1016/j.cpb.2020.100157
142. Soares, A.; Ramos, S.; Albergaria, T.; Delerue-Matos, C. Green zero valent iron nanoparticles dispersion through a sandy column using different injection sequences. *Sci. Total Environ.* **2018**, 637–638, 935–942. DOI: 10.1016/j.scitotenv.2018.05.096
143. Joo, S.H.; Zhao, D. Environmental dynamics of metal oxide nanoparticles in heterogeneous systems: A review. *J. Hazard Mater.* **2017**, 322, 29–47. DOI: 10.1016/j.jhazmat.2016.02.068

144. Singh, J.; Singh, A.V. Microbial strategies for enhanced phytoremediation of heavy metal-contaminated soils. In *Environmental pollutants and their bioremediation approaches*. CRC Press, **2017**; pp 257–272. DOI: 10.1201/9781315173351-4
 145. Wang, T.; Lin, J.; Chen, Z.; Megharaj, M.; Naidu, R. Green synthesized iron nanoparticles by green tea and eucalyptus leaves extracts used for removal of nitrate in aqueous solution. *J. Clean Prod.* **2014**, *83*, 413–419. DOI: 10.1016/j.jclepro.2014.07.006
 146. Yi, Y.; Wei, Y.; Tsang, P.E.; Fang, Z. Aging effects on the stabilisation and reactivity of iron-based nanoparticles green synthesised using aqueous extracts of *Eichhornia crassipes*. *Environ. Sci. Pollut. Res.* **2019**, *26*, 28361–28371. DOI: 10.1007/s11356-019-06006-z
 147. Manquían-Cerda, K.; Cruces, E.; Rubio, M.A.; Reyes, C.; Arancibia-Miranda, N. Preparation of nanoscale iron (oxide, oxyhydroxides and zero-valent) particles derived from blueberries: Reactivity, characterization and removal mechanism of arsenate. *Ecotoxicol. Environ. Saf.* **2017**, *145*, 69–77. DOI: 10.1016/j.ecoenv.2017.07.004
 148. Dong, H.; He, Q.; Zeng, G.; Tang, L.; Zhang, C.; Xie, Y.; Zhang, C.; Xie, Y.; Zeng, Y.; Zhao, F.; Wu, Y. Chromate removal by surface-modified nanoscale zero-valent iron: Effect of different surface coatings and water chemistry. *J. Colloid. Interface Sci.* **2016**, *471*, 7–13. DOI: 10.1016/j.jcis.2016.03.011
 149. Garcés, V.; Palencia, M.; Combatt, E. Development of bacterial inoculums based on biodegradable hydrogels for agricultural applications. *J. Sci. Technol. Appl.* **2017**, *2*, 13–23. DOI: 10.34294/j.jsta.17.2.11
 150. Dong, H.; Lo, I.M.C. Influence of calcium ions on the colloidal stability of surface-modified nano zero-valent iron in the absence or presence of humic acid. *Water Res.* **2013**, *47* (7), 2489–2496. DOI: 10.1016/j.watres.2013.02.022
 151. Jung, B.; O'Carroll, D.; Sleep, B. The influence of humic acid and clay content on the transport of polymer-coated iron nanoparticles through sand. *Sci. Total Environ.* **2014**, *496*, 155–164. DOI: 10.1016/j.scitotenv.2014.06.075
 152. Joshi, N.; Filip, J.; Coker, V.S.; Sadhukhan, J.; Safarik, I.; Bagshaw, H.; Lloyd, J.R. Microbial reduction of natural Fe(III) minerals; toward the sustainable production of functional magnetic nanoparticles. *Front. Environ. Sci.* **2018**, *6*, 127. DOI: 10.3389/fenvs.2018.00127
 153. Yiming, S.; Jassby, D.; Zhang, Y.; Keller, A.A.; Adeleye, A.S. Comparison of the colloidal stability, mobility, and performance of nanoscale zerovalent iron and sulfidated derivatives. *J. Hazard Mater.* **2020**, 122691. DOI: 10.1016/j.jhazmat.2020.122691
 154. Cross, R.K.; Tyler, C.; Galloway, T.S. Transformations that affect fate, form and bioavailability of inorganic nanoparticles in aquatic sediments. *Environ. Chem.* **2015**, *12* (6), 627. DOI: 10.1071/en14273
 155. Watts, M.P.; Coker, V.S.; Parry, S.A.; Patrick, R.A.D.; Thomas, R.A.P.; Kalin, R.; Lloyd, J.R. Biogenic nano-magnetite and nano-zero valent iron treatment of alkaline Cr (VI) leachate and chromite ore processing residue. *J. Appl. Geochem.* **2015**, *54*, 27–42. DOI: 10.1016/j.apgeochem.2014.12.001
 156. Dong, H.; Lo, I.M.C. Influence of humic acid on the colloidal stability of surface-modified nano zero-valent iron. *Water Res.* **2013**, *47* (1), 419–427. DOI: 10.1016/j.watres.2012.10.013
 157. Garrido-Ramírez, E.G.; Theng, B.K.; Mora, M.L. Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions – A review. *Appl. Clay. Sci.* **2010**, *47* (3–4), 182–192. DOI: 10.1016/j.clay.2009.11.044
 158. Semerád, J.; Cajthaml, T. Ecotoxicity and environmental safety related to nano-scale zerovalent iron remediation applications. *Appl. Microbiol. Biotechnol.* **2016**, *100* (23), 9809–9819. DOI: 10.1007/s00253-016-7901-1
 159. Yu, G.H.; Kuzyakov, Y. Fenton chemistry and reactive oxygen species in soil: Abiotic mechanisms of biotic processes, controls and consequences for carbon and nutrient cycling. *Earth. Sci. Rev.* **2021**, *214*, 103525. DOI: 10.1016/j.earscirev.2021.103525
 160. Tang, W.W.; Zeng, G.M.; Gong, J.L.; Liang, J.; Xu, P.; Zhang, C.; Huang, B.B. Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials. *Sci. Total. Environ.* **2014**, *468–469*, 1014–1027. DOI: 10.1016/j.scitotenv.2013.09.044
 161. Kappler, A.; Straub, K.L. Geomicrobiological cycling of iron. *Rev. Mineral Geochem.* **2005**, *59*, 85–108. DOI: 10.2138/rmg.2005.59.5
 162. Labille, J.; Brant, J. Stability of nanoparticles in water. *Nanomedicine.* **2010**, *5* (6), 985–998. DOI: 10.2217/nnm.10.62
 163. Sravanthi, K.; Ayodhya, D.; Swamy, P.Y. Green synthesis, characterization and catalytic activity of 4-nitrophenol reduction and formation of benzimidazoles using bentonite supported zero valent iron nanoparticles. *Mater Sci. Technol.* **2019**, *2*(2), 298–307. DOI: 10.1016/j.jmset.2019.02.003
 164. Bardos, P.; Merely, C.; Kvapil, P.; Koschitzky, H.P. Status of nanoremediation and its potential for future deployment: Risk-benefit and benchmarking appraisals. *Remediation : the journal of environmental cleanup costs, technologies & techniques.* **2018**, *28* (3), 43–56. DOI: 10.1002/rem.21559
 165. Corsi, I.; Winther-Nielsen, M.; Sethi, R.; Punta, C.; Torre, C.D.; Libralato, G.; Lofrano, G.; Sabatini, L.; Fiordi, L.; Cinuzzi, F.; Caneschi, A.; Pellegrini, D.; Buttino, I. Ecofriendly nanotechnologies and nanomaterials for environmental applications. *Ecotoxicol. Environ. Saf.* **2018**, *154* (15), 237–244. DOI: 10.1016/j.ecoenv.2018.02.037
 166. Sanchez, Y.; García-Quintero, A.; Palencia, M. Determination and distribution of size of inorganic particles by spectral deconvolution of surface plasmon resonance. *J. Sci. Technol. Appl.* **2018**, *5*, 45–54. DOI: 10.34294/j.jsta.18.5.34
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