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GREEN CHEMISTRY FOR CHEMICAL SYNTHESIS

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ABSTRACT

Modern trends in the greener synthesis and fabrication of inorganic, organic and coordination compounds, materials, nanomaterials, hybrids and Nano composites are discussed. Green chemistry deals with synthesis procedures according to its classic 12 principles, contributing to the sustainability of chemical processes, energy savings, lesser toxicity of reagents and final products, lesser damage to the environment and human health, decreasing the risk of global overheating, and more rational use of natural resources and agricultural wastes.Greener techniques have been applied to synthesize both well-known chemical compounds by more sustainable routes and completely new materials. A range of man-sized materials and composites can be produced by. Greener routes, including nanoparticles of_metals, non-metals, their oxides and salts, aerogels or quantum dots. At the same time, such classic materials as cement, ceramics, adsorbents, polymers. Greener approach: This utilizes heating aniline, zinc dust in acetic acid for 2 hrs. Further reaction mixture is poured in water and crystals are collected by filtration. This method does not involve acetic anhydride, hazardous solvent, less waste products.

1 THEORY[1-2]

1.1 Introduction[3-4]

The term Green chemistry offered to the scientific community in 1991 was designed. For elimination or decrease in hazardous substances, trying to reduce the exposure of humans and environment to. Chemicals. Currently, several green processes are applied for water purification, energy generation and fabrication of electronics, medicines, plastics and pesticides, among many other goods. As a main idea, any chemical substance possesses hazardous properties, caused by their internal (molecular) structure, which can be changed/modified. The types of hazards are the following: physical hazards (flammability, explosive properties); toxicity (mortal, cause of cancer or other illnesses); and global hazards (decrease in ozone layer, change of climatic conditions, overheating, etc.). Green chemistry deals with synthesis procedures according to its 12 key principles, without or at least with reduced negative impact on human health and environment. These principles, to be effective, need to be applied simultaneously. An absolutely Green synthesis does not exist: as an alternative, Greener synthesis is more truthful definition.

Greener approach: This utilizes heating aniline, zinc dust in acetic acid for 2 hrs. Further reaction mixture is poured in water and crystals are collected by filtration. This method does not involve acetic anhydride, hazardous solvent, less waste products.

2 METHODOLOGY[4-5]

General synthesis methods of green chemistry are

2.1.1 Physical and Chemicals Methods[4-5]

2.1.1.1 BALL MILLING[4-5]

Chemical reactions can be efficiently driven by mechanical energy via ball milling, belonging to the mechanochemical (tribochemical) synthesis, widely used in organic chemistry, in addition to classic applications in inorganic solid-state processes. As an example of equipment, Retch planetary-type high-energy ball mill is described. The use of ball milling allows us to increase energy efficiency and, at the same time, avoid toxic reagents and solvents. These reactions, as well as MW-assisted. Processes, take place without the use of solvents and at room temperature. Being simple and environmentally friendly, the ball milling is also considered as a green tool for chemistry, but it is not. Used in a widespread manner by chemists, despite its big potential. Among other reactions, carried out. by ball milling, are those with the use of solid oxidants and reluctant for oxidation and reduction purposes, respectively, dehydrogenate coupling, synthesis of polymers, amino acids and peptides, coordination compounds, composites ‘cellulose-plastic’, asymmetric organic reactions using catalysts for particular organic chemistry reactions.

2.1.1.2 MICROWAVE IRRADIATION[6-7]

This is a green source of heating both in organic and inorganic synthesis, based on the conduction and dipolar polarization. A series of organic molecules have been reported as obtained this economic, efficient, fast and clean way, now recognized as a conventional synthetic chemistry tool, which has made a great contribution to organic synthesis. MW energy is non-ionizing radiation, which does not influence on the molecular structure of compounds. The MW coupling of a substance depends on its dielectric constant, so N, N-dimethylformamide (DMF), methanol, acetone, and water is rapidly heated under MW irradiation, in a difference from CCl4, toluene or aliphatic hydrocarbons. The electromagnetic energy, being transformed into heat, drives interactions between compounds. MW irradiation and reaction components are in a direct interaction, so a minimum of energy is needed for. It's heating, without expanding the process to the furnace material. That is why the temperature profiles of congenitally and MW-heated simplesare different (in the MW case, the interior is hotter. and the surface is cooler). The heating is uniform and takes place volumetrically, in all the sample; the heat transfer requires lesser energy due to thermal conduction inside the sample. The MW heating is almost instantaneous, very fast, due to the fast transfer 'MW energy—heat', and can be stopped. Immediately by a simple turn-offof the MW equipment. In addition, the MW heating is selective, since reagents possess distinct capacity to be MW-heated, allowing, for example, the heating active points in a sample instead of heating an entire sample. MW heating has the following advantages, among others, beingcompared with conventional heating: fast process speed, pure products, lesser heat loss, high heating efficiency, less waste, low cost of operations, lesser possibility of side products. Solvent- free (dry media) conditions of MW-assisted reactions are preferable, to avoid fast uncontrolled solvent heating and violent explosions. Precursors can be. Adsorbed on inorganic supports, transparent for microwaves (montmorillonite clays, zeolites, ceramics, Al2O3, SiO2) or, on the contrary, possessing strong MW-absorbance (for example, graphite). These. Supports can also contain additional reagents or catalysts. MW-assisted solvent-free reactions on inorganic supports at relatively low bulk temperature have shown certain advantages in the processes of reduction and oxidation, DE protection and protection, condensation, rearrangement, heterocyclic synthesis, etc. leading to important products such as HCN, imines, nitro alkenes, examines, among others Modern apparatus for MW heating is well developed and covered in a comprehensive review; a commercial example is a reactor Mon wave. For simple experiments, modified domestic MW ovens are frequently used. Commercial equipment includes SMC (apparatus with single-mode cavity, 0.2–80 ml volume of sealed vessels), CEM MARS multimode MW reactor and Milestone Flowsynth continuous-flow reactor, all with maximum pressure of 300 psi.

2.1.1.3 PHOTOCATALYSIS[8-9]

Photochemical reactions under UV-irradiation are considered as green chemistry interactions and are based on the electronic excitation, which influences the chemical reactivity of reagents in organic Synthesis. A mechanism of photo catalysis describes generation of singlet oxygen and its role in. the photo-oxygenation (in corporation of molecular oxygen into molecules), combination of photochemical processes with enzyme catalysis, application of continuous flows or micro reactors for their optimization.

2.1.1.4 HYDRO (SOLVO) THERMAL SYNTHESIS[10-11]

A solution reaction-based approach is applied to synthesize compounds, crystallize and grow single crystals and polycrystals at high pressures (normally up to 10 bar) and elevated temperatures (generally up to 300°C) in water or organic solvent media. The equipment for hydro(solvo)thermal technique consists of an autoclave (thick-walled steel cylinders, sometimes with protective inserts made of Teflon, platinum, titanium, quartz, gold, etc.), containing solvent (water) and dissolved/ suspended precursors. A combined equipment ‘microwave-hydrotherma treatment’ has been frequently used in laboratories. The main advantage of the hydrothermal method is the possibility of the formation of crystalline phases, unstable at the melting point of the desired compound; the main disadvantage is the necessity to have expensive equipment. Morphology control and crystallinity for the formed materials can be made by changing pressure, temperature, solvent, reaction time or precursors’ ratio. Hydrothermal reactions in water are considered as more suitable for green chemistry purposes, being environmentally friendly, and are widely applied to fabricate a variety of materials. This method allows minimum loss of reactants and frequently higher yields of products, being especially useful to obtain classic and less- common nanostructures with desired shape and size control products.

2.1.1.5 ULTRASOUND-ASSISTED (SONOCHEMICAL) SYNTHESIS[12-13]

Ultrasound-assisted (sonochemical) synthesis is only a solution-based approach (since cavitation occurs only in liquids) working as a result of the phenomenon of the acoustic cavitation (bubbles, appearing in aliquid, grow and implosively collapse, leading to extreme local pressures of 1000 atm and temperatures of 5000 K) in a liquid phase, without a direct affectation to the bond vibrational energy. Chemical reactions can be started or intensified in these conditions, additionally to the formation of free radicals and H2O2. Chemical composition, reactivity and surface morphology of materials (frequently increasing surface area) can be considerably changedas a result of these collisions.

2.1.1.6 MAGNETIC FIELD ASSISTED SYNTHESIS[14-15]

Magnetic field-assisted synthesis is currently studied as an alternative to traditional methods. Because some of the traditional methods require the use of toxic solvents or additional steps that need more energy and can generate unwanted residues. These extra steps can be omitted using magnetic fields. During the synthesis of the desired material. The synthesis assisted by magnetic fields allows obtaining morphologies different from those prepared by traditional methods. In addition, it is possible to influence the orientations of the final product planes. Some synthesis techniques where the assistance of magnetic fields can be used are the methods of coprecipitation,solvothermal, electrospinning, etc. In addition, the magnetic field assistance can be implemented directly in the solution to influence the growth of the crystals of the desired material and can be applied for the formation of thin layers of some composites. The synthesis assisted with magnetic fields has numerous advantages due to its simplicity; however, it has some important limitations, derived from the foundation of the technique, because it can only be applied to materials whose reactants or products have magnetic properties; that is why the vast majority of reports in the literature use magnetic iron oxides.

Iron oxides such as Fe3O4 can adopt different assisted morphologies with magnetic field; for example, it is possible to obtain complex Fe3O4 nanorods by the solvothermal technique. This is possible because, during the formation of nanorods, the growth of the crystals of the metal oxideis oriented in a specific orientation due to the magnetic field. If the magnetic field is applied in theFe3O4 synthesis by thermal decomposition, it is possible to obtain nanotubes of 250 nm, which arenot formed in the absence of the magnetic field; besides, it was observed that the speed in which these nanoparticles of Fe3O4 are heated by hyperthermia is considerably higher in the oxides synthesized in the presence of the magnetic field. Another example that can be mentioned of the synthesis of Fe3O4 with the assistance of magnetic fields is a series of chains prepared at a temperature of 90°C. These particles had an average size of 150 nm. This was achieved due to the growth of the particles of uniaxial way by the influence of the magnetic field, and it was observed that the intensity of the magnetic field during the synthesis had a significant effect on the anisotropy of the resulting material. The assisted syntheses with magnetic fields can also be applied to the synthesis of some composites, as long as they comply with the characteristics mentioned above. An example of this is the thin layers of reduced graphene oxide (rGO) with Fe3O4 nanocrystals. The synthesis of this composite is quite simple, based on taking advantage of the ferromagnetic characteristics of the nanocrystals of Fe_3O_4 that are adhered to the surface of sheets of rGO. When applying the magnetic field on this suspension, the particles agglomerate in one of the walls of the reactor and they adhere to each other by the electrostatic interactions.

2.1.2 Biological Methods[16-17]

Biological methods, being compared with conventional chemical and physical methods, could bea preferable synthesis route due to environmentally friendly conditions, despite their lower speed of metal reduction. However, their studies are currently relatively limited, especially those establishing key factors of the biosynthesis, so this method is only developed in laboratory scale, although bacteria could be applied for industrial recovery of silver. The biological synthesis of nanoparticles does not require further stabilizing agents: the microorganisms or extracts themselves act as stabilizing and capping agents. Other advantages of the biological routes are no necessity of toxic chemicals and contaminants, possibility to control shapes and sizes, low cost, biocompatibility and numerous precursors (microorganisms and plants). So, biological methods perfectly fit to the green chemistry, in particular to nanochemistry, resulting in biologically produced nanoparticles, which are non-toxic, stable, environmentally friendly and cost effective. Frequently, the nanoparticles, prepared by biological methods, expose a higher antimicrobial activity (being compared with those synthesized by conventional chemical methods), related with the fact that the stabilization and capping by proteins in more effective. Main recent reviews inthis area are described. Biology-based green chemistry methods consist of the use of bacteria, viruses, yeasts, plant extracts fungi and algae, among which we consider plant extracts as most frequent and popular green routes, as it will be shown below especially for the synthesis of nanoparticles, not only those of noble metals, but also carbon dots, metal sulfides, oxides, etc. This area, phytonanotechnology (use of plants) is scalable and medically applicable. Microorganisms represent natural nanofactories, capable to adsorb, accumulate and reduce toxicity of heavy metals, where enzymes are able to reduce metal ions to cero-valent nanoparticles. In the case of bacteria use for nanoparticle preparation, the techniques include the use of bacteria-containing biomass, as well as supernatant and derived components. Mycosynthesis (use of fungi) allows an easy, stable and possibly scaled-up biosynthesis of nanoparticles. Viruses, whose feature is dense and highly reactive surface (for instance, the surface of tobacco mosaic virus contains 2130 capsid protein molecules), were used to produce several inorganic nanoparticles, such as CdS, ZnS, Fe_2O_3 and SiO_2, important for semiconductor and quantum dot (QD) applications. In addition to conventional 0D nanoparticles, the nanotubes and nanowires can also be produced by virus action. The use of yeasts led the preparation of CdS and PbS QDs, Au and other metal nanoparticles. The use of algae is rare, generally for Au, Pd and Pt nanoparticles. Thus, in the case of algae use, the tetrahedral, decahedral and icosahedral Aunanoparticles, as well as bimetallic Ag/Ag nanoparticles, can be formed due to the action of proteins as stabilizing agent, shape-control modifier and reductant at the same time. Inorganic micro- and nanosized materials can be prepared via intracellular- and extracellular microorganism-assisted synthesis. The formation of nanoparticle is considered (but not yet fully understood) as a bottom-up process due to redox processes with participation of metal ions and biological molecules (proteins, sugars and enzymes), provided by the microorganism, whose interaction with metal ions depends on its type and can vary, also depending on temperature and pH (environmental factors), as well as metal salt concentration, leading to a particular morphology and size of nanoparticles. In the intracellular methods, several additional stages are needed, such as ultrasonication to destroy cell wall, washing, centrifugation, etc. which are absent in the extracellular techniques. Biosynthesis processes of fabrication of homogeneous-size nanoparticles with certain reproducible morphology is carried out by size and shape control of critical factors, such as temperature (maximum possible for fast growth of microorganisms), pH (one of the most important factors, ranged generally from 3 to 10; acidic pH contributes to the agglomeration of nanoparticles due to the higher ion binding), salt concentration, choice of biological source, temperature ,redox conditions, synthesis duration and incubation period, irradiation and aeration.As it was noted, the use of plant extracts are common preparation procedures for a variety of nanoparticles of metals, non-metals and several of their compounds. Plant extracts contain polyphenols, terpenoids, proteins, enzymes, peptides, sugars, phenolic acids, bioactive alkaloids as a driving force for nanoparticle formation. Using plant extracts, the following nanoparticles have been obtained: Au, Ag (a host of reports), Cu, CuO, TiO2, ZnO, In2O3, Fe, Fe2O3, Pb and Se. A large number of their final morphologies have been reported: spheres, triangles, cubes, pentagons, hexagons, wires, rods, etc., for example, Au triangles (reduction of HAuCl4 with Aloe vera), and Ag nanowires (reduction of Ag+ withCassia fistula leaf). Nanoparticle sizes can vary considerably, for example, CdS (from ultra-small 2–5 nmto large 200 nm), Ag (5–400 nm), Au (5–85 nm) or magnetite (20–50 nm). Factors influencing their size and shape are as follows: plant extract and metal salt concentrations, temperature (25–95°C), pH (lower pH—larger particles), reaction time (normally from minutes to several hours). Different metals have distinct capacity to be reduced by plant extracts; easiest processes correspond tonoble metals, especially silver. Typical disadvantages in plant-assisted reduction of metals are difficulties in separation of formed metal nanoparticles from the biomass and accompanying putrification processes in reaction systems in the case of long-term reduction. So, the low or practically no cost of plant extracts can cause an imagination about apparent scalabilityfor these processes.

2.2 GREEN SYNTHESIS OFORGANIC, LABELLED AND HYBRID COMPOUNDS[19-20]

2.2.1 REACTIONS THEORY[19-20]

Reactions play the most fundamental role in synthesis. The ideology of Green Chemistry calls for the development of new chemical relativities and reaction conditions that can potentially provide benefits for chemical syntheses in terms of resource and energy efficiency, product selectivity, operational simplicity, and health and environmental safety.

2.2.1.1 ISOMERIZATIONS[22-23]

Isomerization of propargyl alcohols into conjugated carbonyl compounds provides an atomeconomic means for synthesizing such compounds. By using a ruthenium-catalyzed redox isomerization of propargyl alcohols into enones in lieu of the traditional twostep stoichiometric reduction and oxidation sequence, a catalytic enantioselective total synthesis of adociacetylene B can be realized efficiently. Isomerization of an alkynyl vinylcyclopropene to a fused 5- to 7-ring structure converts classical atom inefficient synthetic strategies to ones of ideal atom, economy.

2.2.1.2 ADDITION REACTIONS[24-25]

The processes of adding allyl alcohol to alkynes to form unstaturated ketones and aldehydes in aqueous media were developed by Trost et al. And Dixneuf et al, respectively. Another elegant example was recently reported byKrische and coworkers, in which primary alcohols were added stereoselectively to alkenes, which provides an atom economic version of the classical reaction where a Grignard reagent is added to an aldehyde.

2.2.1.3 Direct Conversion of C–H Bonds[27-28]

Direct transformation of the C–H bonds of organic molecules into desired structures without extrachemical transformations represents another class of major desirable reactions. In nature, a varietyof organic compounds can be oxidized easily by molecular oxygen or other oxygen donors in the cells of bacteria, fungi, plants, insects, fish, and mammals. It is worth noting the important advances in biomimetic approaches to such oxidations. Hydroxylation of linear alkanes or methane to generate terminal alcohols is very useful in the synthesis of chemicals and fuels. However, the direct conversion of C–H bonds into C–C bonds leads to more efficient syntheses of complex products with reduced synthetic operations. Recently, great progress has been made in transition-metal-catalyzed activation and further reaction of C–H bonds. Li and others have developed various methods to generate C–C bonds directly from two different C–H bonds in the presence of an oxidizing reagent through a cross dehydrogenative coupling (CDC) catalyzed by transition metals. For example, (NH)-indoles and tetrahydroisoquinolines were converted directly into alkaloids by using such a coupling.

2.2.1.4 SYNTHESIS WITHOUT PROTECTIONS[29-30]

Because of the nature of classical chemical reactivity, organic synthesis extensively utilizes protection–deprotection of functional groups, which increases the number of steps in synthesizing the desired target compounds. Novel chemistry is needed to perform organic synthesis without protection and deprotection. Recently, progress has been made on this subject. For example, Baran et al. have re-ported a total synthesis of a natural product without any protecting groups. Another instance is the efficient synthesis of ()-3-deoxy-D-glycero-D-galacto- nonulosonic acid (KDN) by using the indium-mediated allylation reaction in water reported by Chan and Li. The Knoevenagel condensation of the diketone with hemiacetalic sugar gave-C-glucosidic ketone in water directly. The Click chemistry developed by Sharpless tolerates a wide range of functionalities and allows the direct modification of biological compounds. The archetypical example of Click chemistry is the Huisgen 1, 3-dipolar cycloaddition of alkynes to azides to form 1, 4-disubsituted 1, 2, 3-triazoles catalyzed by Cu (I). The reaction is mild and highly efficient, and does not require protecting groups.

2.2.1.5 TANDEM/CASCADE/FLOW REACTOR[31-33]

Also of fundamental importance to greener syntheses is the development of tandem and cascade reaction processes that incorporate as many reactions as possible to give the final product in one operation. For example, a palladium-catalyzed tandem reaction resulted in multirings in one step. Another example is Jamison’s synthesis of the core piece of ‘‘ladder’’ polyether marine natural products through a biomimetic cascade cyclization in neutral water. An alternative way to simplify organic syntheses into a single operation is to perform sequential reactions in a flow reactor. Ley and colleaques reported that a multistep synthesis of the alkaloid natural product (-)- oxomaritidine can be accomplished by using microfluidic pumping systems that pass material through various packed columns containing immobilized reagents,catalysts, scavengers, or catch- and-release agents, combining seven separate synthetic steps linked into one continuous sequence.

2.2.2 METAL SALTS, COMPLEXES AND MOFS[34-35]

In the case of using alkaline and alkaline-earth metal complexes as final products or reactants, high-purity, highly thermally stable, crystalline and blue photoluminescent bis (8-hydroxyquinoline) calcium (CaQ2) was prepared with high yields from 8-hydroxyquinoline and Ca (OH) 2 (2: 1 molar ratio) in water by stirring at 90°C for 4 h, being proposed for use as organic electroluminescent materials. Another example is an improved method for transformation of meseylates or glycidyl tosylates to allyl alcohol derivatives, applying excess amount of reducing agent rongalite (approx. 3 mol equivalent, sodium hydroxymethanesulfinate dihydrate Na+ HOCH2SO2 – · 2H2O) with catalytic amount of tellurium (0.1 mol equivalent) as catalyst material. The purpose was to avoid difficulties in elimination of elemental tellurium, formed from telluride anion, during this conversion, resulting in excellent yields (up to 92%). This process can be considered as greener due to the recyclability of tellurium and its use in small catalytic amount, conversion of rongalite (commercially available, inexpensive and powerful reagent for organic synthesis) to bisulfite derivative, which is non-toxic and water-soluble, and use of water as principal solvent with addition of small volume of tetrahydrofuran (THF). For metal phthalocyanines as important compounds with a host of applications, new sustainable synthesis methods are in a permanent search. In general, industrial production of phthalocyanines requires relatively high temperatures (above 180°C) and hazardous solvents. Phthalocyanines in a crystalline form are of especial interest. Thus, prism-shaped crystals of cobalt phthalocyanine (CoPc, more than 1 mm in size, stable up to 430°C) and zinc phthalocyanine (ZnPc, up to 8 mmin size, stable up to 550°C, prepared at 160°C from o-phthalodinitrile and metal acetates as precursors for 6 h in one-stage solvothermal process, using EtOH, pentanol or benzyl alcohol as reaction media. Change of solvent led to different length of phthalocyanine needles. This greener technique does not require any additional substances, in particular surfactants, or recrystallization with the use of concentrated sulfuric acid. Since MPc single crystals are important materials for construction of devices, among other applications, the search for appropriate environmentally friendly methods for their synthesis and growth contributes to rapid development of organic semiconductor devices. Greener synthesis of MOFs is also underway in several laboratories worldwide. In relation to green chemistry, the crucial parameters in the MOF synthesis consist of: (i) solvent, (ii) cation source (inorganic part), (iii) linker molecules (organic part), and (iv) synthesis conditions (pressure, temperature, reactor). In the case of wastes in MOF syntheses,their big amounts are formed as a result of solvent use both in the synthesis and for purification purposes; therefore, greener solvents are needed, for instance, ethanol or acetic acid. Maximum use of all precursors should be taken into account: any waste or side product should be re- elaborated that leads to the loss of time and energy. Metal oxides or hydroxides (lesser sulfates) are recommended to be used as metal source, thusavoiding loss of toxic anions (perchlorates, nitrates or chlorides) due to water formation from O atoms of oxides and protons from acidic linkers. Solvent-less and energy-minimized methods are preferable, routes for synthesis and purification of crude MOFs. Organic linker molecules from renewable natural products (biomass) are desirable, for example, cellulose or starch (the same for solvents: water or ethanol). All additional unnecessary steps should be avoided, for example, temporary modification of processes. Aniline along with Zinc and acetic acid is the key reaction as it gives the part of Oxides.

2.2.3 METAL NANOPARTICLES[33-34]

We will describe the greener methods for obtaining metal nanoparticles. It is worth noting that this field is well developed, first of all, for silver and gold nanoparticles, applying generally biological techniques, lesser for other metals. There are many recent reviews and book chapters inthis field; some selected ones are.

2.2.3.1 General Approach[33-34]

Preparation of nanoparticles, first of all those of elemental metals, has been the central point of green synthesis processes (together with organic reactions discussed above) for the past 15 years. As general approaches for the nanoparticles synthesis, the following aspects are useful in these processes inorder to make them greener. Thus, capping agents are used in the majority ofsyntheses for stabilization, shape control and prevention of aggregation of formed nanoparticles. Classic capping agents in the nanochemistry are long-chain hydrocarbons, functionalized with a heteroatom (oleyamine, trioctylphosphine, oleic acid, and dodecanthiol), polymers (polyvinyl alcohol, PEG) and block copolymers (poly (acrylic acid)-block-polystyrene), dendrimers, etc. For green chemistry purposes, the following agents are considered as greener in the synthesis procedures for nanoparticles formation: (i) polysaccharides (like starch or dextran) exhibiting mild capping ability and water solubility (sometimes reduction properties), avoiding toxic solvents and allowing easy separation of nanoparticles from reaction media; (ii) biomolecules (proteins and peptides) possessing high biocompatibility; and (iii) small molecules (i.e. CO) together with organic capping agents. The natural products, used in the synthesis of nanoparticles and nanomaterials, can be applied not only as capping agents, surfactants, solvents and reactants, but also as carriers, catalysts and templates. The use of ligands can passivate and coat nanoparticle surfaces, thus stabilizing them, preventing agglomeration and influencing their chemical properties. Typical ligands in the nanoparticle synthesis are phosphines, thiols, amines, selenols, carbenes and alkynyls, being classified by their molecular structures and 'head group'. Classic reducing agents in nanoparticle synthesis are normally N2H4, HCOH and NaBH4. Ascorbic acid as an organic reductant can be also used. The following greener reductants are recommended for safer obtaining nanoparticles: (i) molecular H2 (disadvantage: combustibility); and (ii) polysaccharides (used also as capping agents, see above) like b-D-glucose, starch or amylose, possessing water solubility and avoiding hazardous organic solvents. NaAlH4 and other strong reductants contribute to the formation of small nanoparticles, whereas plant extracts result in polydisperse products and larger particles. Their use is directly or indirectly related with toxicity, since non-toxic (green) reductants are not so strong in order to be able to form metal nanoparticles of sufficiently high quality, where a much faster kinetics is needed. On the other hand, strong reductants are frequently toxic and expensive. So, one of the main purposes of green synthesis of high-quality nanoparticles is the search for or creation of green (non-toxic) and simultaneously strong reductants. In the case of solvents, whose consumption in some manufactures, for example, pharmaceutical industry, is over 80%, their correct selection is highly important, taking into account the high amount of used solvent wastes and their toxicity. Solvents are applied for dissolution of raw materials/ reactants, heat transfer, dispersion and solubilization of formed nanoparticles. So, the following solvents are recommended as greener media fornanoparticle low- and large-scale synthesis: (i) obviously water as preferred solvent (if, for any reasons, it is impossible to carry out a solvent-less synthesis as the best option), always available at low cost and non-flammable (disadvantage: high heat capacity, inhibiting energy-saving production), and (ii) SC fluids (CO2, H2O and ILs). In the cas of SC water (critical pressure 22.1 MPa, critical temperature 646 K), the SC hydrothermal synthesis is controllable and economically preferable; in addition, SC water is able to dissolve organic substances and to obtain nanoparticles, highly dispersible in organic media. In the case of SC CO2 (SC pressure 74 bar, SC temperature 304 K), it is also promising, being non-flammable, non-toxic, compatible with the environment, chemically inert and inexpensive. ILs, consisting of charged organic and inorganic ion pairs, can substitute toxic and volatile organic solvents; in this case, capping agents are generally unnecessary. The use of ILs can be united with microwave (due to high dielectric constants, high polarities and high ionic charges) and ultrasonic treatment. Among greener synthesis strategies for nanoparticle synthesis, in addition to correct selection of solvents, capping agents and reductants, the selection of heating method is also important to avoid high energy consumption. Furnace, oil/water bath and heating mantle are classic heating sources, which can be replaced by microwaves, whose aid has already led to preparation of a series of nanoparticles (metals, metal chalcogenides, phosphates, oxides, etc.). Solvent-less MW-assisted route is preferable or, in the case of impossibility, the use of DMF or DMSO (sometimes, additional small IL amounts are useful), possessing high dielectric constants, is recommended. Larger nanoparticles are normally synthesized at prolonged MW-irradiation time. Ultrasound-assisted synthesis of nanoparticles is also considered as green method, where the heating is produced fromacoustic cavitation and not directly from ultrasound itself. Ultrasonic treatment allows also maintaining formed nanoparticles to remain small without fast further agglomeration. After preparation, nanoparticles are normally separated from reaction medium by precipitation and washed by their redissolving and precipitation. Post-processing can include size sorting. Greener syntheses of nanoparticles, in particular, are carried out by biological methods,where reducing agents are organic compounds and biomolecules.

2.2.3.2 NOBLE METAL NANOPARTICLES[35-36]

Nanoparticles of metallic silver and gold have been prepared by green methods much more in comparison with other noble and other metals with aid of bacteria, fungi, plant extracts, yeasts, viruses and algae. In the synthesis of Ag nanoparticles, a variety of the following physical methods (accompanied by chemical reduction of Ag+ ion to convert it to Ag0) have been applied: UV- and sunlight photo reduction (leading mainly to large nanoparticles and nanocrystals; long-term acting stabilizing agents required), ultrasound-assisted processes (temperature control is needed), laser ablation (leading to nanoparticles with perfect shapes and sizes), microwave-assisted reactions (stabilizing agents required), radiolysis, electrochemical reduction and high-pressure (autoclave) technique. Physical methods, used for preparation of silver nanoparticles, have the following disadvantages: tube furnace (large space, heating environment), ceramic heater (fast cooling needed), laser ablation (depends of laser characteristics) and arc discharge (use of Agwires as electrodes). Also, Ag0 nanoparticles were prepared by chemical routes using the following reductants, among others: NaBH4, sodium citrate, ascorbic acid, curcumin, heparin, polyblock polymers and polysaccharides, as well as thermal decomposition of AgNO3 via spray pyrolysis. These reactions are different in respect ofnanoparticles. As example of green synthesis of noble metal nanoparticles, a simple use of ascorbic acid as a reducing agent and sodium carboxymethylcellulose as a structure-directing agent, one-dimensional Ag nanobelts (lengths of 50 µm) and other nanostructures (brick-like, pie-like and three- dimensional hierarchical ones) were prepared from AgNO3 at large scale in mild conditions at 30°C and used for catalytic purposes. As a result of classic action of polyphenol- type compounds, Au nanoparticles (16.6 nm, diverse shapes) were prepared with the aid of catechin (a polyphenol compound, belonging to flavonoids) as a reducing and capping agent. In the case of algae as green medium], both microalgae (Chlorella vulgaris, Chaetoceros calcitrans, Spirulina platensis, Oscillatoria willel, Plectonema boryanum) and macroalgae (Sargassum cinereum, Padina pavonica, Caulerpa racemosa, Ulva lactuca) were used for Ag0 nanoparticles synthesis. Plant extracts have been extensively used for fabrication of Au and especially Ag nanoparticles (interest caused by the antibacterial properties of Ag nanoparticles). In some reactions, Phoenix dactylifera seeds (as waste product), Taraxacum officinale, Cassia tora L. roots, C. longa tuber, soya bean leaf (Glycine max) and Hippophae rhamnoides (Pd nanoparticles) extracts were applied, among many others. In addition, Ag nanoparticles (from AgNO3) and TiO2 nanoparticles (from TiO (OH)2) were prepared using aqueous leaf extract of Euphorbia prostrata. Also, spherical Ag (12 nm) and hexagonal and triangular Au (11 nm) nanoparticles were obtained with the aid of leaf extract of Rosa rugs in water for 10 min].

2.2.3.3 NON - METAL ELEMENTAL NANOPARTICLES[37-38]

Practically, all reports on non-metals in elemental state, obtained by green chemistry methods, are related with carbon nanosized allotropes: nanorods with fluorescent properties, nanotubes, graphene and its oxidized forms, as well as some hybrids. Selected recent reviews in this field are described. These nanoparticles have been mainly prepared by hydrothermal, microwave, pyrolysis of plants or their wastes, plant-extract-assisted techniques or their combinations. Varieties of these combinations are especially well seen in the example of carbon dots/QDs, additionally providing their water-solubility properties. Thus, fluorescent carbon nanorods (CNDs, red emission peak at 615 nm, quantum yield 15%) were synthesized by microwave treatment of a non-fluorescent p-phenylenediamine in EtOH-H_2O solution leading to its carbonization and formation of CNDs. These CNDs serve as chemo sensors for glutathione (GSH) detection and temperature sensor at a molecular level. Alternatively, MW-assisted pyrolysis of reagents was applied for preparation of highly fluorescent N-doped carbon dots of 5 nm size from sesame seeds(8.02% quantum yield), exhibiting water-soluble properties and suitable for Fe (III) selective sensing. Aqueous fluorescent carbon dots (size range 3.14–4.32 nm) were hydrothermally synthesized from turmeric and black pepper, red chili, cinnamon and sweet potato peels. As a result, it was confirmed that the C dots' toxicity strongly depends on the method of their fabrication, being studied in human cancer cells (gliobastoma) in a range (0.1–2 mg ml−1) of concentrations. Red chili-derived C dots showed higher toxicity, being compared with citric acid- derived C dots, revealing that the selective toxicity is caused by the presence of functional groups on their surface. The obtained self-fluorescent C dots can be tracked inside cells and exploited for imaging in vitro. Water-soluble fluorescent carbon quantum dots (CQDs) (quantum yield 46.6%) were hydrothermally prepared also from Tamarinds indicia leaves and applied for Hg2+ sensing in the range from 0 to 0.1 mm These bio-compatible CQDs can be potentially applied in diagnostics of diseases, bio-imaging, sensing, etc. As examples of using other plant extracts, fluorescent water-soluble N/P co-doped CQDs were hydrothermally prepared at 90–150°C from edible Eleocharis delis, resulting in easily scalable CQDs serving as sensors for Fe3+ ions and having potential applications in an anti-counterfeit area. The Pontiac ficus-indica extract, having hydrophilic properties, was used for ultrasound-assisted preparation of laminar carbon fromcommercial graphite as a precursor for 30 min. Small QDs were obtained from the same precursorby stirring for 30 min at 50°C and further ultrasonic treatment for 30 min more. In addition, water-soluble photoluminescent CQDs (size 1–3 nm, quantum yield 14%) were hydrothermally obtained from lemon peel waste and applied for Cr6+ detection (limit 73 NM). This fabrication method can be scaled up. The composite of these CQDs with TiO_2 is capable to carry out photo catalytic degradation of MB dye, having catalytic activity 2.5 times more being compared with TiO_2 nanowires due to a better charge separation on the interface in the hybrid, and the sweet potatoes are considered as waste materials from which carbon nanorods with a diameter of 2.0 ±0.6 nm can be obtained with a quantum yield of 8.9%, which when coated with (3-aminopropyl) triethoxysilane to be used as an ecofriendly sensor for ox tetracycline detector, with a detection limit of 15.3 nag ml−1. In the case of graphite oxide (Grow)-graphene (G)-GO conversions, active substances in plant extracts lead to the reduction of GO or Grow forming rGO or graphene. Thus, graphene was prepared by Grow reduction using Cocoas nucifera L. (coconut water) under sonication for 1 h and further heating at 80–100°C for 12–36 h. RGO nanosheets, functionalized with polyphenol, were prepared according to the Hummers method by action of Catullus colocynths leaf extract as stabilizing and deoxygenating agent. In these conditions, rGO nanosheets are not subjected to further agglomeration and, in addition, were found to possess a dose-dependent toxicity against DU145 cells. Extracts of carotenoids available in vegetables (sweet potato, carrot, etc.) were used for GO reduction in aqueous NaOH medium at 90°C under sonication, leading to the sp2 carbon atom restoration. Also, structural changes of GO shape can occur. Thus, GO tubes of micrometer length, having irregular three-dimensional network forms, were obtained by a metal-complication route by GO cross-linking with Zn, Ca and Sir chloridesin water in a temperature range 24–55°C for 2 h. Ca2+ coordination required a higher temperature than Zn2+ and Sr2+. Such composites can be applied in the biomedical field, for example, GO tubes and sheet with calcium alginate, showing a considerable mechanical improvement in comparison with GO. There are several reports on the growth of carbon nanotubes (CNTs) using plant extracts as catalysts; however, high temperatures are requiring for their formation. Thus, CNTs were grown using rose (Rosa), garden grass (Condon dactyl on), walnut (Jungians regain) and name (Azadirachta indicia) plant extracts in methanol, loaded in a Si sample, as catalysts by chemical vapor deposition (CVD) of acetylene gas at 575°C; meanwhile, carbon nanobelts and SWCNTs were obtained at 800°C (not in cases of all extracts). The products did not contain toxic metals; this is a great advantage of this greener method. As an example of green-chemistry-produced CNT composites highly thermally stable carbon nanotubes/polyaniline (CNT/PANI) hybrids, useful for modification of electrodes on nickel foam basis, were prepared by aniline polymerization of aniline in multi-walled carbon nanotube (MWCNT)-COOH presence in water and ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [BF4]) as green solvents and mineral acids (HCl and HNO3). Polymer layer was found to be coated with CNTs. Other non- metal nanoparticles are rare, for instance, 28 nm P nanoparticles obtained from tricalcium phosphate (Ca3P2O8) as precursor salt by employing Aspergillius tubingensis.

2.2.4 MATERIALS, NANOMATERIALS, COMPOSITES AND HYBRIDS[39-40]

A lot of investigations have been carried out, applying green chemistry routes, where possible, to synthesize various hybrids, materials and composites. The greener chemistry methods have been developed, in particular for titanium and manganese oxides, metal and metal oxide by hydrothermal and microwave-assisted techniques, as well as reflux. Apart, several important green procedures have been offered for important types of materials as polymers and their composites, ceramics and bioceramics, cement, adsorbents and carbon-based aerogels. In the case of polymers, all 12 principles of green chemistry can be applied specifically to their fabrication, in particular, using agricultural products or wastes as renewable feedstocks instead of coal, natural gas or petroleum, water instead of harmful solvents, at normal pressure and room temperature, as well as other conditions with minimum pollution and risk of accidents. For the greener synthesis of polymers, the following substances can be used as renewable starting materials cardanol, renewable plant oils, itaconic anhydride and lactic acid, meanwhile natural lipase enzyme can be used as catalyst in the polymerization processes. As an example of a water-assisted procedure, the porous, stable, hydrophobic and high-surface-area polymer hybrids, possessing a host of phenolic hydroxyl groups, were prepared from m-trihydroxybenzene and 4, 40 -diaminobiphenyl as precursors in water via azo coupling, encapsulating magnetic $Fe3O4@SiO2$ nanoparticles in polymer matrix, and further freeze-drying. In respect of methylene blue as a model contaminant, this composite, due to its extensive conjugated system, revealed high adsorption capacity (1153 mg g−1), easy magnetic recovery from water and minimum five times of reuse maintaining the same adsorption properties. Particles of Au and Ague Nano composites were prepared in water at room temperature using core–shell micro gels based on poly (N-isopropyl acrylamide)/polyethylene mine (Pinal/PEI) These micro gels possess a role of templates and reductants, when Au (III) ion in HAuCl4 3H2O is first reduced resulting in Au0 nanoparticles, which are stabilized by PEI shells and then act as seeds for the formation of bimetallic nanoparticles. The formed Nano composite was used as catalyst for p-nitro phenol reduction resulting in p-aminophenol, revealing their 25-fold higher performance compared with simple Au nanoparticles. Related stable raspberry-like polymer colloids, decorated with Ag nanoparticles (up to tens of nanometers in size, depending on metal precursor concentration, quantity of polymer and reaction time) in a raspberry-like fashion, were obtained in EtOH solution by the interaction of polymer spheres and silver nitrate without additional stabilizers, showing good antibacterial properties. Fabrication of emerging polymers made with or containing elemental sulfur is an important issue in respect of waste re-elaboration contributing to sustainability, since sulfur is a side product in the oil industry. Special attention is paid to the polymerization reactions of renewable monomers (i.e. triglycerides and terrenes) with sulfur, which can be processed without solvent use, according to the green chemistry principles; polysulfide products applied for energy storage, photo catalytic water splitting and remediation of heavy metals. These processes can be carried out by low-temperature polymerization (inverse vulcanization) in molten sulfur with control of the structure of formed-containing polymers. One of the approaches is related with possible interactions in water as green solvent, involving inorganic polysulfides such as Naps- [S]n-Snag and their interaction with polymer particles suspended in water as dispersion. The resulting polymers can contain up to 75% sulfur. Another option is the use of SC CO_2 in these processes. Meanwhile, S_8 is non-toxic, the lack of knowledge on polysulfide's toxicity should also be taken into account, as well as necessary investigations on their recyclability, scalability and DE polymerization back to monomers. At the same time, such sulfur containing polymers can be biodegradable, since the S–S bond is subjected to photolysis and reduction. Highly flexible polyurethane (PU) soft foams from Kraft lignin by its liquefaction in microwave-assisted conditions, using castor oil and polypropylene glycol trial as chain extenders. Other possible applications of this material can be the decrease of glass transition temperature, packaging of furniture and car seats. PU chemistry can be developed by other green processes, for instance, the catalytic reaction of CO_2 with deoxidized soya bean oil as a starting oligomer in a high-pressure reactor (140°C, CO_2 pressure of 1 MPa, 800 p.m.) leads to triglycerides of cyclocarbonate- andepoxide-containing derivatives of carboxylic acids. Also, piperazine-containing bis- phenolformaldehyde polymer was fabricated by a microwave-assisted method. It was revealedthat thispolymer inhibits steel corrosion in HCl by adsorption mechanism. With a similar anti-corrosionpurpose and also for creation of a self-healing coating, the nanocapsules with a natural component, inhibiting corrosion, were prepared by encapsulation of Az. indica in the polymeric shell of ureaformaldehyde under sonication and further polymerization in situ. Green aspects werealsoreported for processes of fabrication of polyvinylchloride (PVC) and several graft copolymersbased on acrylic monomers and starch. Certain attention is paid to biodiesel, bioplastics, and films on their basis and polymer biocomposites. Thus, wood pulp was mechanically disintegrated and oxidized using magnetic Fe@MagTEMPO catalyst (30 nm in size; TEMPO = 4-oxo-2, 2, 6, 6 tetramethylpiperidine-1-oxyl; Fe_3O_4 as a magnetic component; NaClO as oxidant and NaBr as promoter) in water under sonication resulting in nanofibrillatedcellulose (fibre size 5 nm). The role of TEMPO is the diffusion into the fibre walls and oxidation of wood pulp, converting primary hydroxyls into aldehydes and carboxylic acids. The catalyst can easily be recycled and Nalco is transformed to environmentally friendly Nalco, corresponding to the green chemistry principles. Several vegetable waste materials (cauliflower, parsley, carrot and radicchio), without any pre-processing, were converted into biodegradable bioplastics films in aqueous 5% HCl in one-step process at r.t. These films consist of fused cellulose crystals, containing soluble ingredients such as sugars and pectin. Mechanical propertiesof the formed films, completely made of wastes of the vegetables above, are similar to those of starch bioplastics. Antioxidant properties of the original vegetables are conserved in the films due to mild synthesis conditions; the migration into food is low (less than 10 mg dm−2). In addition, itis possible to combine these bioplastics with a variety of other polymers, resulting in newcomposites, for instance, polyvinyl acetate (PVA)-carrot bioplastics, suitable for packaging purposes. Some biocomposites were obtained from recycled bioplastics polylactic acid and treated cellulosicfibres applying MW-irradiation technique combined with enzymatic treatment. This method seems to be very reliable for biocomposites reinforcement, showing an increase in Young's modulus and tensile strength. Also, chitosan cross-linked Ag-containing Nano composites were compared with hag nanoparticles obtained with the aid of garden rhubarb (Rheum rhabarbarum) in respect oftoxicity against HeLa cell line, showing higher toxicity in the last case. Related hyaluronic fibers containing Ag nanoparticles were prepared from alkali solution (NaOH) of natural polysaccharide hyaluronic acid via wet-spinning method (nozzle diameter 0.4 mm), furthercomplexation with Ag+ ions, their reduction and stabilization by the material of fibres under stirringat 80°C. Ag0 nanoparticles were found to be stable for 90 days without aggregation. Thiscomposite material can be applied in dressing purposes, among other possible applications. In addition, biodiesel (methyl or ethyl ester of vegetable oil) was fabricated from several vegetable oilssuch as jawas oil, groundnut oil, soya bean oil, sesame oil, mustard oil and coconut oil. The reactionsteps included the interaction of NaOH with methanol yielding CH_3ONa, its further stirring withgroundnut oil or other oils, and separation of two layers (glycerol and biodiesel). The yield ofbiodiesel was found to be higher in the case of groundnut, soya bean and jawas oil. The area of adsorbents applies green chemistry processes too. It is known that the activated carbon ismostly used for dye removal, but its main disadvantage is high cost. So, cheaper adsorbents are undersearch and development. As green methods for the fabrication of adsorbents for dye removal from wastewater, the ultrasonication, microwave-assisted processes and use of ILs are considered as suitable to satisfy the 12 rules of green chemistry. In addition, a variety of functionalization (physical, chemicaland biological) methods is known to improve their efficiency, providing faster adsorption interactions. Resulting composites can contain minerals, nanostructurized metals and other nanomaterials, magnetic additives, polymers.

3 RESULTS

A range of nanosized materials and composites can be produced by greener routes, including nanoparticles of metals, non-metals, their oxides and salts, aerogels or QDs At the same time, such classic materials can be improved or obtained by cleaner processes as cement, ceramics and bioceramics, adsorbents, polymers, bioplastics, biodiesel and biocomposites. All methods from the above discussed set of greener laboratory techniques cannot be always considered as indeed green upon scaling up. As an example, ball milling in a larger scale could be a source of solid microsize pollution. In organic chemistry, the green chemistry reactions include several processes in the formation of C–C bonds (i.e. Suzuki and Glaser coupling, Knoevenagel condensation, McLurry, Wittig, Gewald, Michael, Reformatsky and Gringard reactions, arylaminomethylation, etc.), C–N bonds (synthesis of oximes, imines, azines, guanidines, (thio)semicarbazones, nitrones,N-arylation of amines, etc.), C–O, C–S, C-Hal, C–H and other bonds, cycloaddition reactions, reductions and oxidations, as well as for. Functionalization of nanocarbons (CNTs, graphene and C60) and in supramolecular chemistry. A range of nanosized materials and composites can be produced by greener routes, including nanoparticles of metals, non-metals, their oxides and salts, aerogels or QDs. At the same time, such classic materials can be improved or obtained by cleaner processes as cement, ceramics and bioceramics, adsorbents, polymers, bioplastics, biodiesel and biocomposites. Our future challenges in resource, environmental, economical, and societal sustainability demand more efficient and benign scientific technologies for. Working with chemical processes and products. Green chemistry addresses. Such challenges by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes and apparatus that can simplify operations in. chemical productions, and seeking greener solvents that are inherently environmentally and ecologically benign. Together, such fundamental innovations in chemical sciences will lead us to a new generation of chemical syntheses.

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4 CONCLUSION

The green chemistry methods include several non-contaminating physical methods as microwave heating, ultrasound-assisted and hydrothermal processes or ball milling, frequently in combination with the use of natural precursors, which are of major importance in the greener synthesis, as well as solvent-less and biosynthesis techniques. Biological methods (the use of bacteria, viruses, yeasts, plant extracts, fungi and algae) perfectly fit to the green chemistry, in particular to Nano chemistry, resulting in biologically produced nanoparticles, which are non- toxic, stable, environmentally friendly and cost effective. Plant extracts contain polyphenols, terpenoids, proteins, enzymes, peptides, sugars, phenolic acids and bioactive alkaloids as a driving force for nanoparticle formation. It is important to highlight that green chemistry and the awareness that this has given to the scientists has allowed us to make exhaustive revisions of the traditional methods to optimize them and to implement them based on the standards of the presenttime and, in some cases, the traditional methods have been substituted, bringing as a consequence more optimized processes both at the laboratory level and at the industrial level.

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