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ARTICLE

Half a Decade Progress of Biomass-assisted Development of Zirconium Nanomaterials: Anti-microbial Potentials

D. Kar Mahapatra[a], **A. G. M. Haldar**[b], **K. M. Dadure**[c] and **R. G. Chaudhary**[d]

[a] *Department of Pharmaceutical Chemistry, Dadasaheb Balpande College of Pharmacy, Nagpur 440037, Maharashtra, India.*

[b] *Department of Applied Chemistry, Priyadarshini Bhagwati College of Engineering, Nagpur 440009, Maharashtra, India.*

[c] *Department of Chemistry, J. B. College of Science, Wardha 442001, Maharashtra, India.*

[d] *Post-graduate Department of Chemistry, S. K. Porwal College, Kamptee, Nagpur 441001, Maharashtra, India.*

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Abstract: Nanotechnology has revolutionized all fields across the globe and opened up several frontiers in nanobiotechnology, nanopharmacotherapeutics, material and applied sciences, biomedical sciences, drug delivery, tumor therapy imaging, biosensing, electronics, bactericidal activity, catalysis, optics and photoelectrochemistry. Nature has provided abundant biological resources to synthesize NPs eco-friendly. Over the past few years, purified extracts of bacteria, fungi, algae, seaweeds and viruses have received adequate attention for the development of energy-proficient, non-toxic, economic nanoparticles (NPs). The present review article exclusively focuses on the last 5 years (January 2016 to December 2020) progress in the area of green synthesis of zirconium nanomaterials (zirconium NPs (Zr-NPs), zirconium dioxide (ZrO_2) and zirconium/metal nanocomposites, Cu/ZrO_2) by utilization of plant extracts, fungal extracts and seaweed extracts. The probable mechanism(s) of the formation of NPs by reduction with bioreductants is (are) also described briefly.

Keywords: Zirconium, Nanoparticles, Plant, Fungi, Seaweed, Anti-microbial potentials.

Introduction

Nanotechnology has revolutionized all fields across the globe and opened up several frontiers in nanobiotechnology, nanopharmacotherapeutics, material and applied sciences, biomedical sciences, drug delivery, tumor therapy imaging, biosensing, electronics, bactericidal activity, catalysis, optics and photoelectrochemistry [1-2].

Diversity of chemical and physical processes has been reported for the synthesis of metallic nanoparticles (NPs) [3]. However, several methods subsisted, but many problems are associated with these processes, like utilizing toxic solvents, expensive production of harmful by-products, …etc [4]. Chemicals, like hydrogen peroxide, hydrazine hydrate, polyvinylpyrrolidone, sodium borohydride, ethylene glycol and dimethylformamide, are generally used for the production of NPs, but they get absorbed on the surface of NPs formed, thereby producing toxicity [5]. Thus, there is a need to explore eco-friendly synthetic protocols for the synthesis of nanomaterials [6-15].

Corresponding Author: D. Kar Mahapatra **Email**: dkmbsp@gmail.com

Nature has provided copious biological resources to fabricate NPs in an eco-friendly manner [16]. With the improvement in technologies, a new way for research and development in the field of biology towards nanomedicine has been ascertained [17]. The use of biological resources in the synthesis of nanomaterials is swiftly developing due to their emergent success, economics, ease of formation and eco-friendly nature [18]. Over the past few years, purified extracts of bacteria, fungi, algae, seaweeds and viruses have received sufficient consideration for the development of non-toxic, economic and energy-proficient NPs [19].

Typically, a bio-organism-mediated metallic salt reduction process occurs when the aqueous extract of the bio-organism reacts with an aqueous solution of the metal salt [20]. The whole reaction occurs at room temperature within a few minutes [21]. Due to the occurrence of an extensive selection of chemicals, the bioreduction process is relatively complex. Biological synthesis of NPs using plant extracts is relatively scalable and less expensive compared with microbial processes [22]. The nature of plant extract, pH, its concentration, temperature, the concentration of metal salt, contact time, …etc. affect the quantity, rate of production and characteristics of the NPs [23]. The source of the plant extract also influences the characteristics of NPs because of varying concentrations and combinations of organic reducing agents. For the green synthesis of NPs, the following points must be considered (i) selecting appropriate bioresources for the reduction of metal salts and (ii) providing optimal reaction conditions for NP formation [24].

The present review article exclusively focuses on the last 5 years (January 2016 to December 2020) progress in the area of green synthesis of zirconium nanomaterials (zirconium NPs, ZrO_2 and zirconium/metal nanocomposites, Cu/ZrO_2) by utilization of plant extracts, fungal extracts and seaweed extracts (Fig. 1). The probable mechanism(s) of the formation of NPs by reduction with reductants is (are) also described briefly.

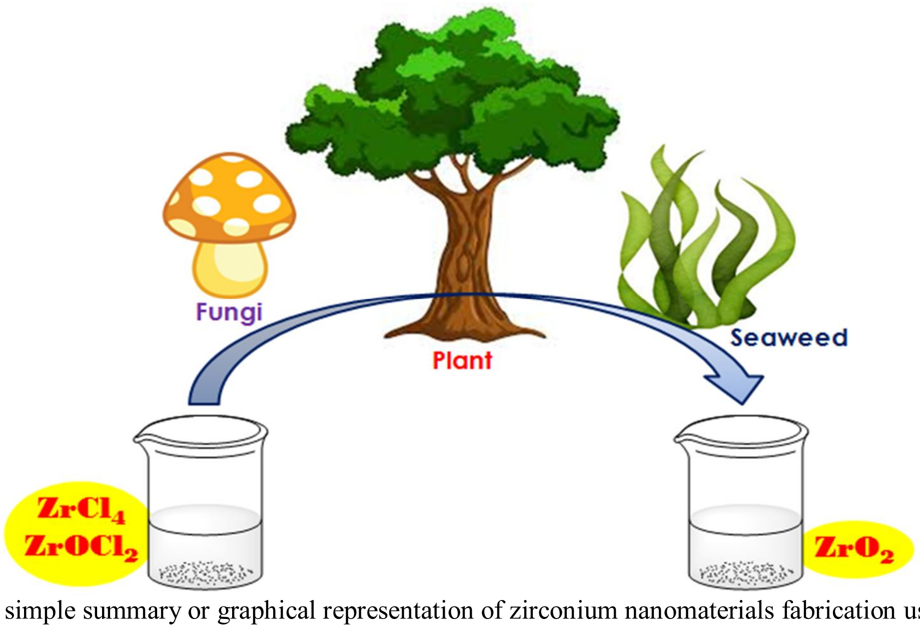


FIG. 1. A simple summary or graphical representation of zirconium nanomaterials fabrication using plant extracts, fungi extracts and seaweed extracts.

Fabrication of Zirconium Nanomaterials

Plant Extracts-mediated Synthesis

The leaf extracts of *Moringa oleifera*, *Rosmarinus officinalis* and *Lagerstroemia speciosa* have been successfully utilized for preparing ZrO_2-NPs of size 9 nm-10 nm (spherical), 12 nm-17 nm (semi-spherical) and 56.8 nm (oval) which presented utility as nanocomposite films, anti-bacterial agents (*Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*) and photocatalytic ally active NPs [25-27].

The root extracts of *Euclea natalensis* were utilized by Silva *et al*. in fabricating ZrO_2-NPs of the size range from 5.9 nm to 8.54 nm and further employed the produced NPs in adsorbing tetracycline for preventing environmental pollution. Sophisticated techniques, such as FTIR, XRD and TEM techniques, have been utilized for characterization [28].

Two plants of the Euphorbiaceae family; *Acalypha indica* and *Jatropha integerrima*, have been reported to play a crucial role in the fabrication of ZrO_2-NPs. Aqueous leaf extract of the former plant was utilized for obtaining cube-shaped NPs of the size range from 20 nm to 100 nm. The NPs were comprehensively characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Energy Dispersive X-ray studies [29].

The aqueous flower extract of the latter plant was employed for obtaining nano-sized materials and characterized by XRD, FT-IR spectroscopy, and UV-Vis spectroscopy. The produced NPs demonstrated better reduction (degradation) of malachite green as compared to conventional reduction [30].

Recently, hybrid ZrO_2-NPs with cerium and copper for multifarious applications has been fabricated through green approaches by model investigators. Nithya *et al*. fabricated agglomerated nano stick-like (20 nm to 45 nm) core metal NPs of CeO_2/ZrO_2 utilizing ionic liquid-mediated *Justicia adhatoda* extract. The bioreductants, such as *N*, *N*-dimethylglycine and vasicinone, present in the extract played a vital role in reducing the ionic form into the elemental form. The hybrid NPs expressed anti-bacterial [higher activity against *S. aureus* (Gram-positive) than *E. coli* (Gram-negative)], anti-oxidant and anti-biofilm (violacein inhibition assay, prodigiosin inhibition assay and biofilm inhibition assay) activities [31].

Similarly, the leaf extract of *Rubia tinctorum* was utilized by Nasrollahzadeh *et al*. for developing Cu/Zr silicate nanocomposite which has a crucial role as a catalyst in the N-benzylation reaction of arylcyanamides. The researchers established the structure of the nanocomposite through techniques, like FESEM, XRD, EDS, BET, FT-IR, TEM and elemental mapping [32].

Azadirachta indica has been utilized for the fabrication of ZrO_2 by two independent groups of Indian researchers. In the former case, the extract produced nano-sized particles that were characterized exclusively by UV-Vis spectroscopy technique with a calculated band gap of 5.80 eV [33].

In another report, the former extract was utilized along with *Aloe barbadensis* in producing nano-zirconium. The authors stated that the obtained NPs showed strikingly high concentration-dependent anti-fungal activity against *Candida albicans*, *Aspergillus fumigatus* and *Aspergillus niger* as evidenced by the zone of inhibition (Fig. 2) [34].

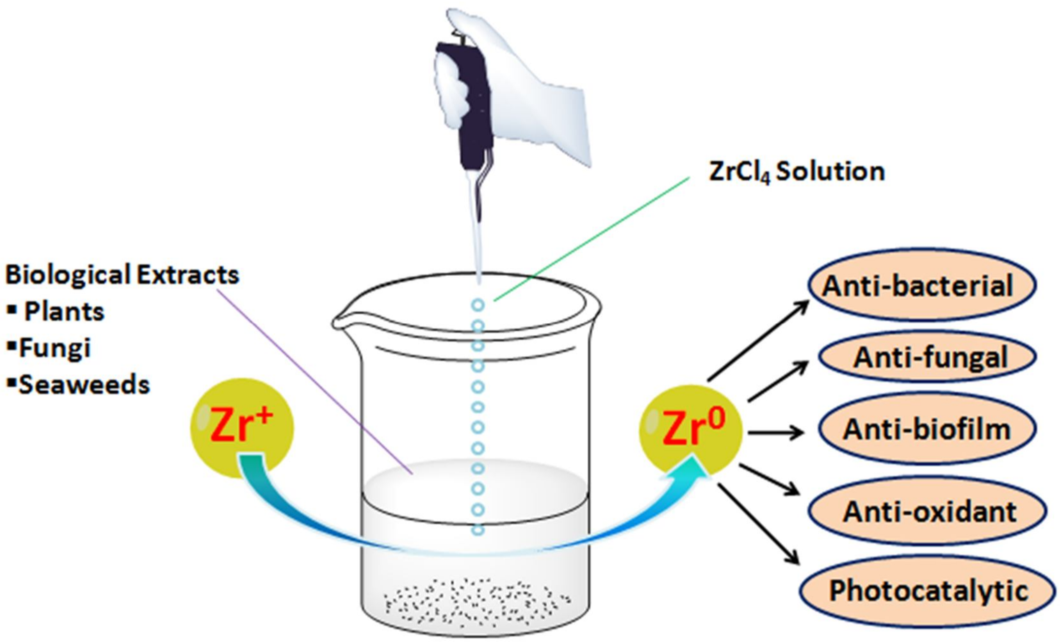


FIG. 2. Formation of zirconium nanomaterials from diverse biomasses and their applications.

Bacteria-mediated Synthesis

Bacteria are having the best biofactory, where several protein-based elements play a pivotal role in the bioreduction processes. They are often regarded as the most trusted comrades for numerous biotechnological products creation in several pharmaceutical industries. However, it is shocking to state that there are no interesting reports available at present for the biosynthesis of ZrO_2-NPs. Though, it is expected that in the near future, enthusiastic researchers will definitely explore the zirconium salt bioreduction potentials of various bacterial species.

Seaweed Extract-mediated Synthesis

Kumaresan and co-workers synthesized tetragonal ZrO_2-NPs of average size of 4.8 nm by utilizing the whole extract of *Sargassum wightii* (Sargassaceae) marine brown algae (Table 1). The prepared NPs were thoroughly characterized through sophisticated analytical tools, such as HR-TEM, XRD, PL spectroscopy, FTIR spectroscopy and UV–Vis spectroscopy. The NPs expressed tremendous anti-bacterial activity against *Salmonella typhi*, *B. subtilis* and *E. coli* with an impressive MIC value. The high bactericidal activity of the NPs is mediated by the large surface area offered by these nanomaterials (Table 1) [35].

TABLE 1. Green synthesized zirconium nanomaterials from various biomasses in the last 5 years.

Biomass	Family	Part used	Type	Size (nm)	Shape	Applications	Ref.#
Acalypha indica	Euphorbiaceae	Leaves	ZrO_2	20-100	Cube	-	19
Aloe barbadensis and *Azadirachta indica*	Meliaceae / Asphodelaceae	Leaves	ZrO_2	350	Spherical	Anti-fungal	24
Azadirachta indica	Meliaceae	Leaves	ZrO_2	-	-	-	23
Euclea natalensis	Ebenaceae	Roots	ZrO_2	5.9-8.54	Spherical	Adsorption of tetracycline	18
Jatropha integerrima	Euphorbiaceae	Flowers	ZrO_2	-	-	Malachite green reduction	20
Justicia adhatoda	Acanthaceae	Leaves	CeO_2/ ZrO_2	25-45	Stick	Anti-bacterial, anti-oxidant and anti-biofilm	21
Lagerstroemia speciosa	Lythraceae	Leaves	ZrO_2	56.8	Oval	Photocatalytic activity	17
Moringa oleifera	Moringaceae	Leaves	ZrO_2	9-10	Spherical	Anti-bacterial	15
Penicillium chrysogenum, *Penicillium pinophilum*, *Penicillium aculeatum*, *Penicillium notatum*, and *Penicillium purpurogenome*	Trichocomaceae	Whole	ZrO_2	< 100	Spherical	Anti-bacterial	22
Rosmarinus officinalis	Lamiaceae	Leaves	ZrO_2	12-17	Semi-spherical	Nanocomposite films	12
Rubia tinctorum	Rubiaceae	Leaves	CuO/ ZrO_2	15-25	Spherical	*N*-benzyl-*N*-arylcyanamides preparation	18
Sargassum wightii	Sargassaceae	Whole	ZrO_2	4.8	Tetragonal	Anti-bacterial	21

Fungi Extract-mediated Synthesis

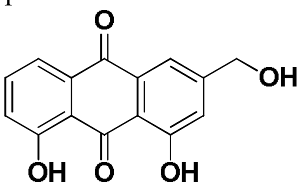
Ghomi and researchers synthesized spherical ZrO_2-NPs through an eco-friendly extracellular development procedure employing various species of Penicillium (*Penicillium pinophilum*, *Penicillium chrysogenum*, *Penicillium notatum*, *Penicillium purpurogenome* and *Penicillium aculeatum*). These biosynthesized NPs were duly characterized through Dynamic Light Scattering (DLS), Fourier Transform Infrared (FT-IR), Atomic Force Microscope (AFM), Energy Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM). The screening of these NPs against a range of Gram-negative bacteria (*S. typhi*, *B. subtilis* and *E. coli*) presented a notable activity owing to smaller dimensions which resulted in a better access to the biological target(s) [36].

Role of Various Phytochemicals in the Bioreduction

Although the precise mechanism of ZrO_2-NP production is unknown, a number of studies strongly suggest that nitrate reductase is a crucial enzyme in NP synthesis in bacteria, with bioreduction being linked to metabolic activities that use nitrate by converting it to nitrite and ammonium [37].

In general, ZrO_2-NPs are made in two steps: first, bulk ions are reduced into NPs and then the produced NPs are capped. The first step in fungal-mediated synthesis includes trapping ions on the surface of the fungal cells and then a 32 kDa protein, which may be a reductase produced by the fungal isolate, reduces ions into NPs. In a later stage, 35 kDa proteins bind to NPs and provide stability [38]. Protein-NP interactions have the potential to help NPs maintain their stability. Fungal proteins play an important role in the reduction of metal salts to their elemental forms. *Volvariella volvacea* proteins are an example of a natural bioreductants. Bioreduction occurs in *Fusarium oxysporum* through NADPH-dependent sulfite reductase (35.6 kDa) and phytochelatin components, while compactin is the bioreductant in *Penicillium brevicompactum* [39-40].

For the formation of ZrO_2-NPs from zirconium salt, the process of bioreduction may be performed by the various prominent phytochemicals (alizarin, aloe emodin, aloin A, aloin B, asiatic acid, azadirachtin, azadirone, betulin, biorobin, corosolic acid, ellagic acid, gedunin, kaempferol, nimbidinin, nimbin, nimocinol, quercetin, ursolic acid and vasicine) present in the plant extract which acted as reducing agent as well as capping agent (Fig. 3). Since plant extracts have hundreds of bioactive components belonging to diverse classes, such as alkaloids, glycosides, proteins, sugars, tannins, anthraquinones, saponins, flavonoids, steroids, terpenes, … etc., there is a possibility that apart from the above-mentioned phytochemicals, some others may take part in the bioreduction process. It is extremely difficult to predict the reducing agent as well as capping agent present in seaweeds and fungi because of large multi-cellular complex system.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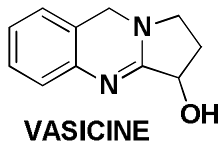
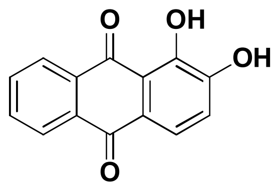
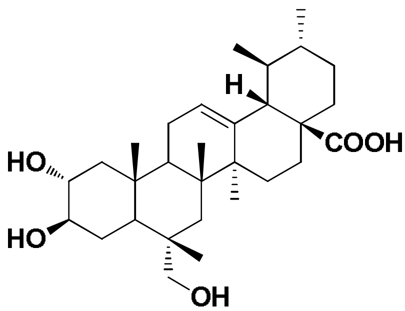
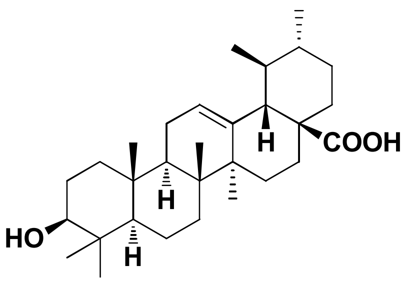

VASICINE


ALIZARIN


ASIATIC ACID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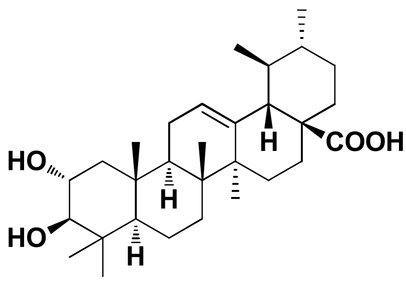
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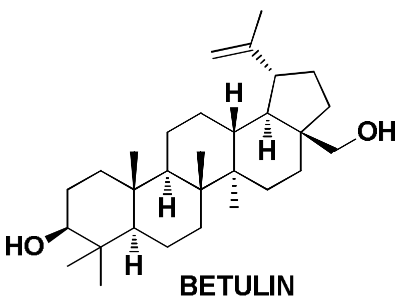
BETULIN

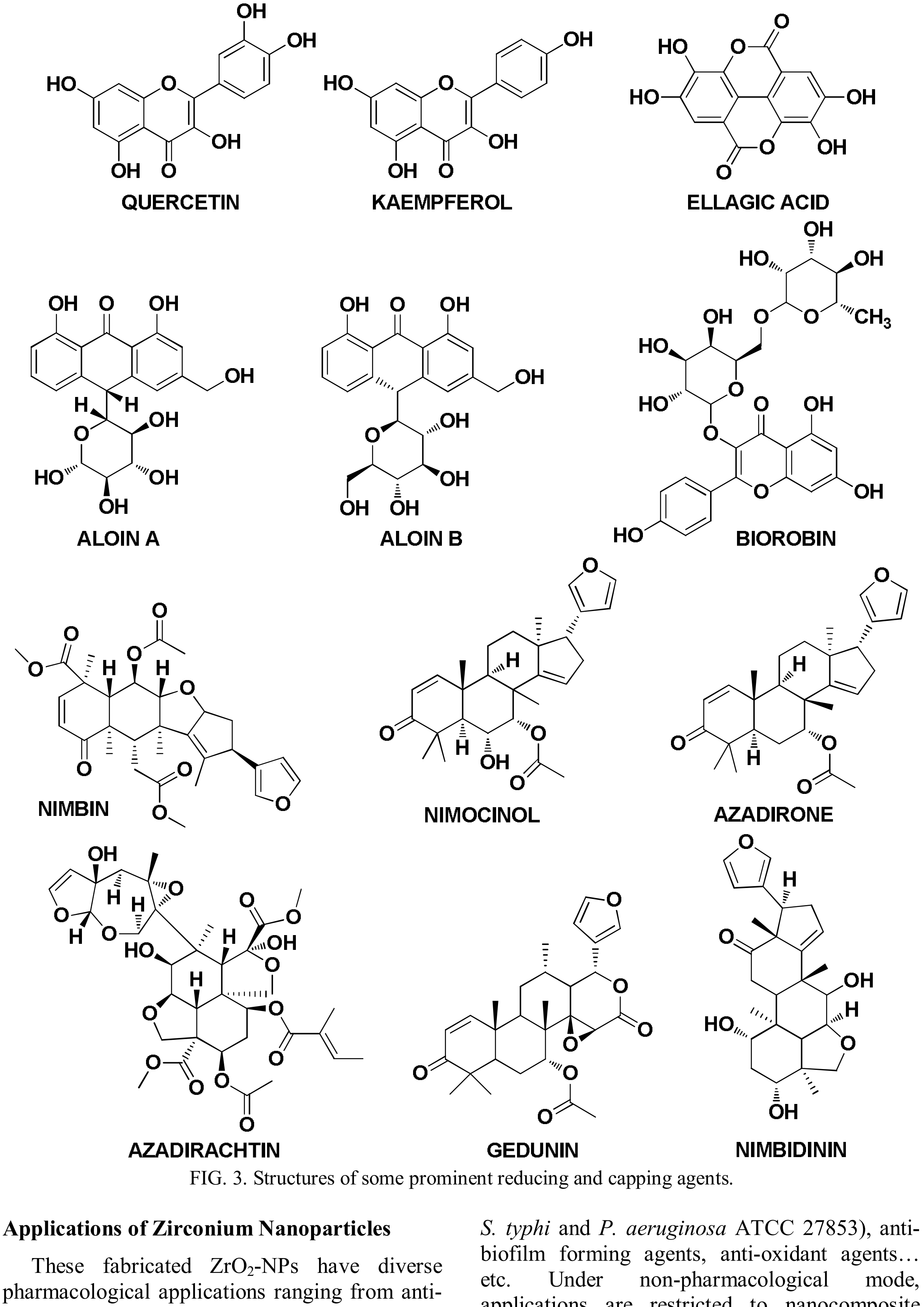

FIG. 3. Structures of some prominent reducing and capping agents.

Applications of Zirconium Nanoparticles

These fabricated ZrO_2-NPs have diverse pharmacological applications ranging from anti-fungal (*A. fumigatus*, *A. niger*, *C. albicans*), anti-bacterial (*S. aureus* ATCC 25923, *S. aureus* ATCC 29213, *E. coli* ATCC 27853, *B. subtilis*, *S. typhi* and *P. aeruginosa* ATCC 27853), anti-biofilm forming agents, anti-oxidant agents… etc. Under non-pharmacological mode, applications are restricted to nanocomposite films, photocatalytic agents, catalysts in *N*-benzyl-*N*-arylcyanamides preparation, assisting adsorption of tetracycline, facilitating malachite green dye reduction and many more.

Conclusion

Nature has provided plentiful bio-resources that can reduce Zr ions into Zr-NPs. In the field of nanotechnology, a reliable and eco-friendly process for the synthesis of NPs is the foremost demand. In order to achieve this goal, the use of natural sources for the green synthesis of NPs becomes crucial. This approach has numerous advantages over conventional methods as a cost-effective, environmentally safe and efficient approach. Though, there are a few shortcomings connected with the biosynthesis of NPs employing green chemistry approach. It is comparatively a slow progression, somewhat complicated to manage the size/shape of NPs employing the biological sources, the precise mechanism for NPs formation is indefinite and non-specific conjugation of proteins/phytoconstituents during the synthesis of NPs. The microorganism (bacteria and fungi)-mediated synthesis is somewhat trouble-free, but there is a need to explore the biochemical and molecular mechanisms of NPs synthesis by these organisms. Algae and seaweeds are comparatively newer bio-resources that are not explored passably and necessitate supplementary exploration. The wide variety of biological activities and imaging properties of biosynthesized NPs may offer a foundation for the progress of future nanomedicine. Additionally, purification and proper characterization of these NPs are the imperative steps to be taken into contemplation before the nanomaterials to be used commercially in healthcare. Despite all the foremost challenges and concerns, the biosynthesized NPs may be potential nanomedicines for the pharmacotherapeutics of a variety of diseases in the near opportunities.

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