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Overview of the plant-based synthesis of metal and metal oxide nanoparticles and their potential application in the formation of protective coatings

Przegląd opartych na surowcach roślinnych metod syntezy nanocząstek metali i tlenków metali oraz ich potencjalne zastosowanie do otrzymywania powłok ochronnych

Technologies for the production of nanomaterials have been developed for many years. Despite the remarkable achievements in this field, nanotechnologies contribute to serious environmental pollution. One of the interesting directions in the search for new, green solutions limiting their harmful impact on nature is the use of plant extracts as substrates in the techniques of synthesis of metal nanoparticles and metal oxides. This article briefly reviews the current state of knowledge on the preparation of metallic nanoparticles via green chemistry synthesis methods. The general mechanism of these processes is presented in an accessible way. In addition, current trends in the field of their use in the formulation of paints and varnishes with antifouling properties and as components of protective coatings preventing corrosion are discussed. A noteworthy way of using metallic nanoparticles in agriculture as a factor inhibiting the negative effects of salinity on the growth of crops was also mentioned. Despite the constantly growing number of scientific reports on these issues, this topic still requires a comprehensive discussion along with a detailed analysis of the synthesis processes. A comprehensive approach will certainly contribute to a better knowledge and understanding of this subject and the improvement of the quality of works devoted to the green synthesis of metallic nanoparticles.

Keywords: biosynthesis, nanomaterials, powder metallurgy, paints, varnishes, protective coatings, green chemistry

Technologie wytwarzania nanomateriałów są rozwijane od wielu lat. Pomimo niezwykłych osiągnięć w tej dziedzinie nanotechnologie przyczyniają się do poważnego zanieczyszczenia środowiska. Jednym z interesujących kierunków poszukiwania nowych, zielonych rozwiązań ograniczających ich szkodliwy wpływ na przyrodę jest wykorzystanie ekstraktów roślinnych jako substratów w technikach syntezy nanocząstek metali i tlenków metali. W artykule dokonano krótkiego przeglądu obecnego stanu wiedzy na temat otrzymywania nanocząstek metalicznych z użyciem metod syntezy biologicznej. W przystępny sposób przedstawiono ogólny mechanizm przebiegu tych procesów. Omówiono ponadto aktualne trendy w zakresie ich wykorzystywania w recepturowaniu farb i lakierów o właściwościach przeciwporostowych oraz jako składników powłok ochronnych zapobiegających korozji. Zwrócono również uwagę na kwestię zastosowania nanocząstek metalicznych w charakterze związków hamujących negatywny wpływ zasolenia na wzrost roślin uprawnych. Pomimo stale rosnącej liczby doniesień naukowych dotyczących tych zagadnień wciąż wymagają one kompleksowego omówienia wraz ze szczegółową analizą przebiegu procesów syntezy. Całościowe ujęcie z pewnością przyczyni się do lepszego poznania i zrozumienia tej tematyki oraz publikowania prac o wysokiej jakości.

Słowa kluczowe: biosynteza, nanomateriały, metalurgia proszków, farby, lakiery, powłoki ochronne, zielona chemia

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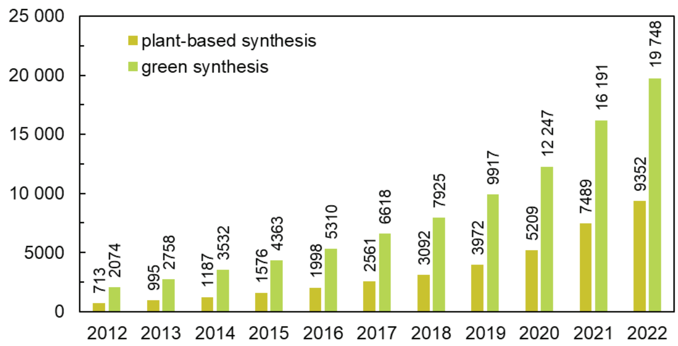

Fig. 1. Number of scientific reports on the production of metal and metal oxides NPs via green synthesis methods using plant raw materials published in the last 10 years

Rys. 1. Liczba opublikowanych w ciągu ostatnich 10 lat doniesień naukowych dotyczących zielonej syntezy nanocząstek metali i tlenków metali z wykorzystaniem surowców roślinnych

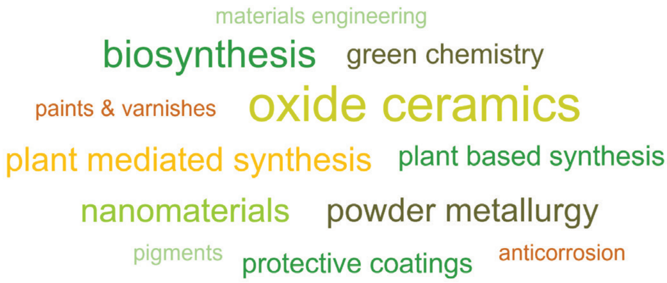

Fig. 2. Green synthesis of metal/metal oxide NPs – keywords cloud

Rys. 2. Zielona synteza nanocząstek metali i tlenków metali – chmura słów kluczowych

1. Introduction

Regardless of tremendous advances in the field of nanotechnology that have been made throughout past decades, new methods for nanomaterials production are still sought. Thus, the development of eco-friendly strategies for nanoparticles (NPs) formation has gained a lot of interest recently. The main reason for this can be attributed to their exceptional properties such as small size, diverse structure, and various application possibilities [1]. Among many well-known raw materials classified as NPs, metal and metal oxides can be distinguished. At present, metallic NPs are produced mainly via chemical reduction methods, which unfortunately require the use of harmful and often toxic substances. This, in turn, contributes to the adverse impact on the environment due to the influence of its pollution or the need for large energy consumption during the synthesis processes [2]. Fortunately, in the world of science, a trend has emerged in conducting the processes of obtaining NPs via green chemistry methods, among which green approaches using plant extracts as reaction substrates should be mentioned. The undoubted advantages of plant-based synthesis methods are their safe nature, neutrality for the environment, low production costs, and the possibility of using a wide range of naturally derived materials. Replacing the classic methods of obtaining metallic NPs with plant-based synthesis allows for significantly reducing or even completely eliminating the use of chemicals (acids, alkalis, organic solvents) that are dangerous or toxic to the environment [3]. Moreover, the final material can be usually formed in a facile process of chemical reduction, sometimes combined with the thermal decomposition of the intermediate product. Such methods are mostly used for the development of metal and metal oxide NPs which hold great potential for application as antimicrobial agents, biosensors, chemical tools in various catalytic reactions (i.e. light-activated processes, pharmaceutical synthesis, green hydrogen production), or corrosion resistant coatings [4].

Despite the abovementioned advantages and undisputed possibilities of the brought up subject, the detailed mechanisms of plant-based syntheses are still not entirely understood [2], and thus some disadvantages still need to be eliminated. At present, the major bottleneck in this topic is often the low efficiency of the processes, which limits the use of the obtained products on a larger scale. Nevertheless, given the growing interest in the improvement of green approaches to the production of metallic materials, this problem may be overcome soon. This can be confirmed by a graph showing the constantly increasing number of scientific reports on this topic (Fig. 1). The graph was prepared based on searching for the phrases "green synthesis" and "plant-based synthesis" followed by "metal/metal oxides nanoparticles" in the ScienceDirect database and collecting the data from the year 2012 till 2022.

This article presents a brief description of the methods for metallic NPs formation along with a review of hitherto scientific achievements in the field of metal/metal oxide NPs green synthesis. Areas of application of the discussed materials as additives to paints and varnishes as well as raw materials for anticorrosive purposes and plant cultivation are introduced. This short review – based on scientific reports published since 2012 – is focused on the development of a green approach for the manufacturing of metallic NPs. The selection of the most relevant keywords made it possible to prepare an overview of research articles. Academic research databases such as ScienceDirect, Scopus, and PubMed were used for the search of appropriate publications. Keywords related to the discussed topic were collected and presented in Fig. 2.

2. Methods for plant-based NPs formation

Green synthesis of plant-based NPs has been under extensive discussion in material science since it holds many advantages over conventional physical or chemical methods of NPs formation. The application of plant extracts has become a unique technology for the synthesis of NPs, as they exhibit dual nature of reducing and capping agents in these processes [5]. Currently, metallic NPs can be usually obtained via two main routes: top-down and bottom-up. The top-down approach is based on physical methods of obtaining materials in the nanoscale by grinding metallic powders with the use of mechanical or electrical energy. Among them, high-energy ball milling, laser ablation, melt mixing or inert gas condensation can be distinguished. Despite the undoubted advantage of these methods, which is the lack of the use of toxic chemicals, they are extremely energy consuming and often require the use of specialized equipment which leads to very high production costs. In addition, controlling the properties of the final material is not easy [6].

In the case of the bottom-up approach, chemical methods and biosynthetic processes can be mentioned. In chemical synthesis, NPs are mainly obtained by sol-gel, hydrothermal, chemical reduction, or precipitation reactions [7]. Such techniques are efficient and easily scaled up, but they require the use of often toxic and environmentally dangerous substrates. Although many reports also discuss easy control over the properties of the obtained NPs in chemical processes, green solutions are constantly being sought. Hence, a trend has emerged in the use of raw materials of natural

Fig. 3. The scheme for the green synthesis of metallic NPs with the use of plant extract

Rys. 3. Schemat zielonej syntezy nanocząstek metalicznych z wykorzystaniem ekstraktów roślinnych

origin as a replacement for hazardous chemical reductants and stabilizers. Biosynthesis uses microorganisms (i.a. bacteria or fungi), biomolecules (i.a. enzymes, carbohydrates), or plant extracts (derived from fruits, vegetables, or flowers). Among them, the easiest in terms of safety conditions and process efficiency is the use of plant extracts as bioreductans [6].

The great advantages of using the plant-based synthesis of metallic NPs are its simplicity, energy saving or availability, and low costs of the raw materials. The general mechanism for the synthesis of metallic or metal oxide NPs from plant extracts is based on the reduction of metal ions by molecules originating from plants such as i.a. polysaccharides, flavones, anthocyanidins, or phenolic acids. The above-mentioned compounds can be easily extracted from almost every plant part – seeds, leaves, roots, stalks, fruits, or flowers – which gives countless possibilities for their use as substrates in the biosynthesis of NPs [2]. Moreover, it is worth mentioning that plant extracts can hold capping, stabilizing, or chelating functions, thanks to which the obtained materials are often characterized with better chemical resistance compared to NPs obtained via chemical methods [1]. The plant-based metallic NPs formation covers three main stages, among which reduction, growth, and stabilization are distinguished. The reduction stage is occurring when metal ions (derived from their salt precursor) undergo reduction through their interaction with compounds contained in plant extracts. Here, hydroxyl groups originating from plant extracts play the main role in the coordination of metal ions and donation of electrons, leading to the reduction process. In the growth stage, the coalescence of small metal NPs into larger particles is occurring. This process is a so-called Ostwald ripening and involves the formation of NPs by heterogeneous nucleation and particle growth followed by further reduction of metal ions. This aggregation is observed due to the stronger bond energy between the atoms of the formed metal compared to the bond energy between the atom and the solvent used in the synthesis (most commonly ethanol, methanol, or water). In this process, the thermodynamic stability of NPs is increased. In the last stage of NPs formation, particles are stabilized. Here, NPs are converted to the most energetically favorable conformation due to the ability of plant extracts to stabilize metallic NPs. The biological activity of compounds contained in extracts increases the stability of the created particles thanks to the presence of groups such as C–C, C=C, C–O, C=O, or O–C=O in their chemical structure. In addition, extracts show capping abilities, thanks to which further growth of particles is limited in the stabilization stage, and the formation of aggregates from metal NPs is prevented [7]. The general scheme for the green synthesis of metallic NPs is presented in Fig. 3.

3. Plant-based synthesis of metal/metal oxide NPs – scientific overview

The development of environmentally friendly methods for the fabrication of metal and metal oxide NPs is an essential step in increasing the importance and changing nanotechnology. In the past decade, many attempts at the plant-based synthesis of metallic NPs were reported in the scientific literature [3]. The growing interest in this field is caused not only because of scientific curiosity and the exquisite properties of obtained materials but also because of the many possibilities given by such methods. However, the undoubted disadvantage of the rapid increase in the number of publications on this topic is the fact that the research is not always discussed in detail. Often there is a lack of thorough and in-depth discussion that includes the synthesis processes optimization or analysis of the impact of reaction conditions on the properties of the obtained materials. Here, a short review based on recent academic reports on the plant-based synthesis of metal and metal oxide NPs will be presented. The green synthesis of materials such as Ag, Au, Pd, Cu, CuO, ZnO, TiO_2, SnO_2, ZrO_2, Al_2O_3, MgO, or CeO_2, as well as a few examples of bimetallic composites, will be included. The most important factors such as morphology and particle size of materials developed in the discussed publications are summarized in Table 1.

Yazdi et al. [8] presented research on AgNPs synthesis with the use of the aqueous flowering shoots of *Allium giganteum* extract. $AgNO_3$ was applied as a metal precursor. The process was carried out at room temperature (RT) and resulted in the fabrication of spherically shaped NPs with a size stated at 4÷35 nm. The reaction has been induced after the extract has been added to 1 mM $AgNO_3$ aqueous solution. The color change of the reaction mixture to light brown (indicating the AgNPs formation) occurred after 24 hours. The obtained material was tested for antimicrobial and photocatalytic activity. It was shown that the biosynthesized AgNPs exhibit great antibacterial activity against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, and *Pseudomonas aeruginosa* bacteria strains.

Okaiyeto, Hoppe and Okoh [9] presented studies on AgNPs development via biosynthesis with the *Salvia officinalis* aqueous leaf extract as a reductive agent and $AgNO_3$ as a metal precursor. Results of morphology analysis revealed the spherical shape of AgNPs with a size of ca. 40 nm. Here, cytotoxicity against human cervix adenocarcinoma cells and antiplasmodial activity against *Plasmodium falciparum* were investigated. In this study, obtained AgNPs demonstrated good antiplasmodial activity and mild cytotoxicity. It was stated that this material can be applied for the development of novel antimalarial drugs and further studies on its activity mechanisms needs to be undertaken.

In the report from Kyzioł et al. [10] research group, an eco-friendly synthesis of AuNPs with the aqueous extract of *Rosa damascene* and $HAuCl_4 \cdot 3H_2O$ (metal precursor) was performed. Reactions were carried in different temperature conditions: at RT and at 40°C. In both cases, obtained particles were mostly spherical, however, their average size varied from 8÷32 nm for AuNPs synthesized at RT and 10÷45 nm for AuNPs synthesized at 40°C. *In vitro* cytotoxicity was investigated and it was proved that the use of obtained AuNPs increases the damage process of cancer cells and can be successfully used for medical applications.

Another study on AuNPs plant-based synthesis was done by Ali et al. [11]. Here, NPs were synthesized with the use of the stalk of an Ayurvedic medicinal plant – *Tinospora cordifolia* – and analyzed for the activity against *Pseudomonas aeruginosa* biofilm formation. Obtained AuNPs were spherically shaped and their average particle size was stated at ca. 16 nm. It was shown that with the increasing concentration of discussed NPs, the *Pseudomonas aeruginosa* biofilm formation decreased which confirmed their potential as antibiotics.

An eco-friendly synthesis of PdNPs using *Filicium decipiens* leaf extract was presented by Sharmila et al. [12] research group. An aqueous solution of $PdCl_2$ was mixed with plant extract and kept in RT for 4 days. The PdNPs formation was confirmed by UV-Vis analysis. Morphology tests showed that obtained PdNPs occurred spherical with size from 2 nm to 22 nm. Results showed that phytochemicals (comprising of amide or amine functional groups) contained in *Filicium decipiens* leaf extract influenced the reduction reaction of Pd precursor resulting in the development of NPs that hold a great antimicrobial activity against Gram-positive and Gram-negative bacteria strains.

Another worth-mentioning research on PdNPs biosynthesis was published by Kalaiselvi et al. [13]. Here, an aqueous solution of $Pd(OAc)_2$ was mixed with alcohol-based *Catharanthus roseus* leaf extract and stirred at 60°C for 10 hours. The reaction mixture was analyzed via UV-Vis spectrophotometry in 1 hour intervals and it was stated that the highest yield in PdNPs formation was recorded at 2nd hour of the performed process. The average particle size was stated at 38 nm and morphology tests confirmed their spherical shape. The presented study showed that the reaction time has a significant influence on the NPs formation and that functional groups contained in plant extract have a critical role in the reduction process and stabilizing the PdNPs.

In the investigation performed by Rajeshkumar et al. [14], CuNPs were synthesized using a rare medicinal plant *Cissus arnotiana* as a reducing agent. It was stated that this extract was used for the first time for the plant-based synthesis of NPs. The prepared plant extract was added to $CuSO_4$ solution and stirred at RT for 4 hours. Here, spherical shaped particles with a size of 60÷90 nm were obtained. The biosynthesized CuNPs showed antibacterial activity against the Gram-negative bacteria (*Escherichia coli*).

In the research from Mali et al. [15], eco-friendly green synthesis of CuNPs using *Celastrus paniculatus* leaves extract was conducted. The reaction mixture was prepared by mixing $CuSO_4$ aqueous solution with an extract solution. The morphology of obtained material appeared spherical shaped NPs with a size between 2 nm and 10 nm. Moreover, it was confirmed that the synthesized CuNPs can be applied as antifungal agents since they showed great antifungal activity against *Fusarium oxysporum*.

Veisi et al. [16] showed a report on a green approach for CuONPs formation using an herbal tea *Stachys lavandulifolia* flower extract. The compounds contained in the extract were used as the reductant without applying harsh chemicals. $Cu(OAc)_2$ was applied as Cu precursor and it was mixed with prepared extract solution at 80°C for 100 min. The formation of CuONPs was confirmed by the change in the color (from yellow to dark brown) of the reaction mixture. The analysis of the chemical composition of the extract showed the occurrence of flavonoids, triterpenoids, steroids, cardenolides, or alkaloids. These, in turn, influenced the reduction of Cu^{2+} ions to CuONPs. Moreover, it was shown that mentioned extract holds a potential as a capping agent which prevents the agglomeration of NPs during the synthesis process. Obtained NPs were spherical with a size of 15÷25 nm.

Naseer et al. [17] presented research on a green route to synthesize ZnONPs. Leaf extracts of medicinal plants *Cassia fistula* and *Melia azedarach* were used as reducing agents and $Zn(OAc)_2 \cdot 2H_2O$ was used as ZnO precursor. Analysis of the extract's chemical composition showed the presence of bioactive functional groups that are responsible for the reduction of $Zn(OAc)_2 \cdot 2H_2O$ to ZnONPs. The change in the reaction mixture color (from brown to white) confirmed NPs formation. Imaging of prepared powders indicated the spherical shape of particles with a size of 3÷68 nm. What's more, the ZnONPs exhibited antimicrobial activity against clinical pathogens which suggests their potential for use in versatile and eco-friendly biomedical product development.

Srinivasan et al. [18] work shows the attempts for the biosynthesized TiO_2NPs via the reduction of $TiCl_3$ using *Sesbania grandiflora* leaf extract. Analysis of extract composition confirmed the presence of alkynes, alkanes, flavonoids, and secondary alcohols which are compounds believed to be involved in the reduction of metal precursors in the formation of NPs. The size of obtained NPs was in the range of 43÷56 nm. Moreover, synthesized TiO_2 samples were studied for their impact on toxicity in zebrafish embryos. It was stated that biosynthesized TiO_2NPs have a great potential application for the use against bacterial pathogens.

An interesting approach for ceramic oxide NPs was reported by Manimaran et al. [19]. In their investigation, SnO_2NPs via microwave-assisted green synthesis with aqueous *Solanum nigrum* leaf extract were prepared. Sn precursor – $SnCl_2 \cdot 2H_2O$ – was mixed with extract solution and subjected to microwave exposure in a domestic microwave oven. The obtained powder was then calcinated at 600°C for 6 hours in order to remove residual post-reaction impurities. Morphology analysis revealed spherical shapes of obtained particles with the average size stated at 45 nm. Further research has shown a protein-like shell surrounding the SnO_2 particles that are responsible for their stabilization.

Da Silva et al. [20] study focused on the development of the green synthesis of ZrO_2NPs using *Euclea natalensis* plant extract. Optimization of reaction parameters covering plant extract and metal precursor concentration, and calcination temperatures was done for, as claimed by the authors, the first time in the literature. The NPs obtained under most optimized conditions were characterized by spherical shape and average particle size of 6÷9 nm.

Detailed research on the influence of different reaction conditions on the properties of green synthesized NPs was also presented in the report presented by Roostaie et al. [21]. Here, mesoporous γ-Al_2O_3 was obtained with the use of *Morus alba* leaf extract. The plant extract was used not only as a reducing agent but also as a biotemplate for the synthesis of the leaf-inspired γ-Al_2O_3. A sol solution of $Al[OCH(CH_3)_2]_3$ was first prepared and then mixed with *Morus alba* extract at different conditions (atmospheric pressure, short and long time contact, vacuum and sonication parameters).

Another metal oxide NPs synthesis was done by Ahmad et al. [22] an eco-friendly method for synthesis in an aqueous environment with the use of *Leucophyllum frutescens* extract was proposed. Obtained NPs occurred to have a particle size of around 34 nm and a cubic structure. Further analysis of the properties of MgONPs showed that they can be considered as green resources for multifaceted environmental (wastewater treatment) and biological (antimicrobial agent) applications.

Sabouri et al. [23] developed a procedure for CeO_2NPs formation via sol-gel reaction with $Ce(NO_3)_3 \cdot 6H_2O$ (metal precursor) and *Rheum turkestanicum* leaf extract (reducing and stabilizing agent). The reaction was carried out by mixing aqueous solutions of Ce precursor and prepared extract for 24 hours at 80°C until the light yellowish color of the solution was acquired. After the process, obtained powders were calcinated at different temperatures (400°C, 500°C, and 600°C). The influence of the temperature of post-reaction calcination on the NPs average size was investigated. It was shown that with increased temperature, the average particle size is also increasing. The CeO_2NPs average size was stated at ca. 12 nm, 24 nm, and 33 nm for calcination at 400°C, 500°C, and 600°C, respectively. This research presents interesting findings on the *Rheum turkestanicum* plant application as a biobased substrate for NPs formation.

A worth mentioning topic in the field of metallic NPs formation is the development of procedures for bimetallic composite synthesis. Emerging interest in this subject is mainly caused by the unique nature of bimetallic NPs which is determined mainly by their complex structure and the occurrence of electronic interactions between metals. Moreover, they stand out with exquisite catalytic, electronic, or optical properties. Thus, bimetallic NPs hold great poten-

Table 1. Overview of the green synthesis of metal/metal oxide and bimetallic composites NPs with the use of different plant sources
Tabela 1. Zielona synteza nanocząstek metali, tlenków metali i kompozytów bimetalicznych z wykorzystaniem różnych źródeł roślinnych

Plant	Metal precursor	Synthesized NPs	Morphology	Particle size [nm]	Ref.
Allium giganteum shoots	$AgNO_3$	Ag	spherical	4÷35	[8]
Salvia officinalis aqueous leaves	$AgNO_3$	Ag	spherical	ca. 40	[9]
Rosa damascene flowers	$HAuCl_4 \cdot 3H_2O$	Au	spherical	8÷32 (RT) 10÷45 (40°C)	[10]
Tinospora cordifolia stalks	$AuCl_3$	Au	spherical	ca. 16	[11]
Filicium decipiens leaves	$PdCl_2$	Pd	spherical	2÷22	[12]
Catharanthus roseus leaves	$Pd(OAc)_2$	Pd	spherical	ca. 38	[13]
Cissus arnotiana leaves	$CuSO_4$	Cu	spherical	60÷90	[14]
Celastrus paniculatus leaves	$CuSO_4$	Cu	spherical	2÷10	[15]
Stachys lavandulifolia flowers	$Cu(OAc)_2$	CuO	spherical	15÷25	[16]
Cassia fistula and *Melia azedarach* leaves	$Zn(OAc)_2 \cdot 2H_2O$	ZnO	spherical	3÷68	[17]
Sesbania grandiflora leaves	$TiCl_3$	TiO_2	triangular, square, spherical	43÷56	[18]
Solanum nigrum leaves	$SnCl_2 \cdot 2H_2O$	SnO_2	spherical	ca. 45	[19]
Euclea natalensis roots	$ZrOCl_2 \cdot 8H_2O$	ZrO_2	spherical	6÷9	[20]
Morus alba leaves	$Al[OCH(CH_3)_2]_3$	Al_2O_3	leaf template	ca. 20	[21]
Leucophyllum frutescens leaves	$MgNO_3$	MgO	cubic structure	ca. 34	[22]
Rheum turkestanicum leaves	$Ce(NO_3)_3 \cdot 6H_2O$	CeO_2	spherical	ca. 12 (400°C) ca. 24 (500°C) ca. 33 (600°C)	[23]
Ginger rhizome powder	$CuSO_4 + AgNO_3$	Cu-Ag	spherical	ca. 59	[25]
	$CuSO_4 + Ni(NO_3)_2$	Cu-Ni	spherical	ca. 68	[25]
	$Ni(NO_3)_2 + AgNO_3$	Ni-Ag	spherical	n/a	[25]
Caccinia macranthera plant	$Zn(NO_3)_2 \cdot 6H_2O +$ $+ Mg(NO_3)_2 \cdot 4H_2O + AgNO_3$	Ag doped ZnO-MgO	spherical	ca. 26	[26]
Sambucus nigra L. shoots	$CuCl_2 + Zn(CH_3COO)_2$	CuO-ZnO	hexagonal (ZnO phase), spherical (CuO phase)	20÷130	[27]

tial in applications for catalysts, sensors, nanoelectronic devices, biomedical tools, or biosensors [24].

Ismail et al. [25] performed research on the preparation of bimetallic composites including Cu-Ag, Cu-Ni, and Ni-AgNPs with the use of ginger rhizome powder as a bioreductive agent. NPs were obtained via two step route. First, the ginger powder was washed with distilled water and dried. Then it was added to aqueous solutions of $CuSO_4$ with $AgNO_3$, $CuSO_4$ with $Ni(NO_3)_2$, and $Ni(NO_3)_2$ with $AgNO_3$. Mixtures were left for 6 hours, filtered, and dried. In the second step, obtained powders were subjected to NaBH4 solution in order to support the reduction process. The change in color of the powder into dark black after the contact with NaBH4 solution indicated the formation of NPs. It was stated that the Cu^{2+}, Ni^{2+}, and Ag^{+} ions were uptaken due to interactions of the hydroxyl functional groups of phenolic compounds found in the ginger powder. The average size of nanocomposites was stated at 59 nm and 68 nm for Cu-Ag and Cu-Ni, respectively. There is no mention of the particle size for obtained Ni-AgNPs. Considering the stated properties, such as excellent absorbance of metal ions, the surface distribution of NPs, outstanding reusability, and stability, such materials have great potential for many industrial applications.

Composite bimetallic nanomaterials synthesis was also presented by Sabouri et al. [26]. Here, Ag-doped ZnO-MgONPs were obtained via a green synthesis approach for the first time in the scientific literature. *Caccinia macranthera* extract was applied as a reducing agent in a reaction with the following metal salts $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 4H_2O$, and $AgNO_3$. First, solutions of Zn and Mg metal salts were mixed in a 1 : 1 ratio for 15 minutes and then 5 wt% of $AgNO_3$ was added and stirred for 30 minutes. In the second step, plant extract solution was added dropwise and the obtained mixture was stirred at 80°C for 6 hours. The final product was calcinated at 700°C for 2 hours. The average particle size of synthesized material was stated at ca. 26 nm and morphology analysis revealed spherical shaped particles. The obtained composite was extensively tested for its potential application as a photocatalyst (for organic dye degradation), cytotoxic agent, or a novel biosensor for Pb^{2+} ions detection.

Cao et al. [27] developed an eco-friendly procedure for another bimetallic composite of CuO-ZnO using *Sambucus nigra* L. extract. NPs were formed in a simple method by mixing the aqueous solution of plant extract with $CuCl_2$ and $Zn(CH_3COO)_2$ at 70°C for 3 hours and then calcinating raw material at 400°C for 6 hours. The morphology analysis results showed that obtained NPs contained polygonal ZnONPs with hexagonal phase and spherical CuONPs with monoclinic phase. The size of ZnO-CuO composite particles varied from 20 nm to 130 nm, depending on the oxide phase. What's more, anticancer activity was also confirmed for the obtained powders.

4. Application potential of green synthesized metal/metal oxide NPs

4.1. General knowledge

While metal NPs (i.a. Ag, Au, Pd, Cu) are most often analyzed as agents for antimicrobial, cytotoxic, or antiplasmodial applications [1], metal oxide NPs are also investigated for their applications as various catalysts, biosensors, or even in tools for electronic devices [3]. Furthermore, one of the widely discussed fields of application of metal and metal oxide NPs is their use as raw materials or additives for the fabrication of protective coatings [28]. Materials derived from natural resources are under constant consideration as green alternatives for anticorrosion or antifouling agents. Plant extracts rich in biologically active compounds hold great potential in this field [29] and their use in the formation of nanomaterials can enhance the protective properties of metallic NPs. Other worth mentioning and rapidly emerging fields for metallic NPs usage are agriculture and plant cultivation. That is because of the stabilization initiated by the compounds contained in the plants, thanks to which, metallic NPs can also exhibit biological activity. This in turn opens the way for their use as inhibitors of the salinity stress in plants [30].

Here, recent advances in the use of biosynthesized metal/metal oxide NPs for the constitution of protective coatings will be briefly discussed. Their application as paint and varnishes components, as well as raw materials for corrosion inhibition will be presented. In addition, a few reports dedicated to the investigation of their inhibiting abilities in plant cultivation will be shown.

4.2. Paints and varnishes

An interesting direction of application of metal/metal oxides NPs produced in the processes of green syntheses is their use as coating materials or components of paints and varnishes with bioactive and/or anti-corrosion properties. A special case of such solutions are the so-called antifouling coatings. The use of these coatings is aimed at inhibiting or a decrease in the formation of biofilm by aquatic organisms, mainly algae, and crustaceans, on the parts of ships underwater. Currently, in industrial practice, mainly Cu-based paints are encountered. Even worse, formulas containing compounds such as mercury and arsenic have also been used in the past. Due to their confirmed harmfulness, solutions that have less impact on the flora and fauna of the seas and oceans are sought [31]. Some of the recent studies covering mentioned topics are presented below.

Alarif et al. [7] presented the research on the antifouling activity of TiO_2NPs synthesized using natural marine extracts. Extracts of two red algae (*Bostrychia tenella* and *Laurencia obtusa*), a green alga (*Halimeda tuna*), and a brown alga (*Sargassum filipendula*) along with a marine sponge sample identified as *Carteriospongia foliascens* were used in the processes of obtaining ceramic particles. The collected algae and marine sponge were air-dried and extracted with methanol. Subsequently, the extracts were filtered, frozen overnight at −10°C, freed from fats, and evaporated to dryness. Titanium (IV) butoxide was used as a Ti precursor, which was mixed with ethanol and aqueous solutions of dried extracts at 50°C for 2 hours, then aged for 24 hours. The resulting gel was dried for 12 hours at 100°C and ground in a mortar, then calcined for 2 hours at 500°C in a muffle furnace. The TiO_2NPs obtained in this way were introduced into the paint formula based on a pigmented mixture of oil binder with Fe_3O_4, ZnO, and polyvinyl chloride (PVC), diluted in xylene. The prepared paint was applied to the steel panels using commercially available paint as reference material. The painted panels were immersed for 108 days in seawater (Eastern Harbor of Alexandria, Egypt) during the spring-summer season. Paints containing TiO_2NPs obtained with *B. tenella* and *C. foliascens* extracts demonstrated an excellent antifouling performance while panels coated with commercial paint were colonized by barnacles.

The above observations were confirmed in the review by Gu et al. [32]. The authors in this article explain that the extracts used by Alarif et al. [7] not only enable the green synthesis of nanomaterials but also inhibit the formation of biofilm. In numerous publications, it is stated that many natural substances of both plant and animal origin have an antifouling effect. It is worth mentioning here: terpenoids, steroids, carotenoids, phenolics, furanones, alkaloids, peptides, and lactones.

The authors also emphasize the influence of the photocatalytic properties of ceramic nanomaterials on increasing the antifouling capacity of the coatings. Nanocrystalline TiO_2 is a material commonly used to modify protective coatings. Due to its ability to generate reactive oxygen species when irradiated with sunlight, it intensifies the antifouling effect of coatings and improves their mechanical strength. This concept was used by Selim et al. [33] by conducting a broad photocatalytic analysis of coatings for ship hulls with TiO_2NPs embedded in a polydimethylsiloxane (PDMS) matrix. Selim et al. [34] continued work on nanoceramics for antifouling applications by developing advanced nanocomposite coatings based on silicone with β-MnO_2 nanorods. The addition of nanowires into the PDMS polymer matrix resulted in obtaining a coating with low surface energy and superhydrophobic properties that prevent the deposition of organisms on its surface.

Another worth-mentioning study on antifouling behavior by green metal/metal oxide NPs was proposed by Lakhan et al. [35]. In their article, they evaluated the antibacterial and antidiatom activity of AgNPs synthesized in a clove bud extract environment. The plant extract was prepared by pouring distilled water and boiling the ground flowers for 20 minutes, then cooling them to room temperature and filtering them through paper filters. The obtained extract was stored at 4°C. For the synthesis of AgNPs, the Ag precursor in the form of $AgNO_3$ was used, and its aqueous solution was mixed with the clove bud extract. After 24 hours of storage in the dark, the mixture was centrifuged for 10 minutes at 8000 rpm and washed with distilled water. The precipitated AgNPs were dried overnight at 60°C. The antibacterial properties were tested using the disk diffusion method, and the activity against *Nitzschia closterium* diatoms was assessed by microscopic determination of the number of microalgae cells on a hemocytometer. The authors showed that AgNPs synthesized in the environment of clove bud extract are capable of inhibiting the multiplication of marine bacterium community and *Nitzschia closterium* diatom.

The use of nano-sized ceramic particles as paint components were also proposed by Solano, Patiño-Ruiz and Herrera [36]. In this paper, they presented research on the use of an aqueous lemongrass extract in the synthesis of TiO_2NPs and ZnONPs. The preparation of the solution proceeded as follows. Cleaned and crushed lemongrass leaves were packed in linen bags and macerated in distilled water for 6 hours. The obtained extract was stored at 4°C. Titanium tetraisopropanolate was used as a Ti precursor. Next, a prepared aqueous extract of lemongrass was added dropwise to the precursor and subjected to ultrasonic treatment for about 30 minutes. The NPs were washed several times with distilled water and ethanol, then centrifuged at 5000 rpm for 30 minutes. The powder was calcined at 550°C for 3 hours to obtain TiO_2 with an anatase structure. Zinc chloride was used as a precursor of Zn, which was dissolved in water extract of lemongrass during 20 minutes of magnetic stirring in a ratio of 80 : 320 v/v. A 5 M sodium hydroxide solution was added to the prepared solution to adjust its pH to 12. The suspension was sonicated and centrifuged at 4000 rpm for 10 minutes. The resulting precipitate was washed with distilled water and ethanol, then finally calcined at 550°C for 5 hours. Ceramic NPs prepared in this way were dispersed in an organic diluent and introduced in concentrations of 2%, 3.5% and 5% w/v% for commercially available enamel paint. The prepared paints were applied to substrates in the form of carbon steel, aluminum, and wood. The authors showed that low concentrations of NPs provide a barrier to corrosion processes. In addition, paints enriched with the addition of TiO_2NPs and ZnONPs have self-cleaning properties and are capable of degrading impurities in the form of methylene blue. Antibacterial activity was confirmed only for ZnONPs.

A different approach, representing composites with green metallic NPs with a ceramic matrix, was presented by Göl et al. [37]. In their work, they proposed the synthesis of AgNPs using black tea (*Camellia sinensis*). The plant extract was obtained in the microwave process by maceration of dried *Camellia sinensis* in 70% ethyl alcohol. Silver nitrate was used as a precursor to the synthesis of AgNPs. The salt was dissolved in the paper-filtered extract with distilled water and sonicated for 48 hours. The resulting precipitate was cleaned with alcohol and air dried, then added to the ceramic glaze. The produced NPs were subjected to microbiological ana-lysis including disc diffusion assay and minimum inhibitors/bactericidal concentration using the broth dilution method. Antibacterial properties of the AgNPs/glaze mixture were tested against *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, and methicillin-resistant *Staphylococcus aureus* bacteria. AgNPs in ceramic glaze showed antibacterial activity reaching up to 90% of lethal effects against both Gram-negative and Gram-positive bacteria. The discussed material has a high application potential as an additive to protective, anti-corrosion, and bioactive ceramic coatings.

4.3. Protective coatings

Although the practical use of green synthesized NPs is still in the development phase, their application as anticorrosion inhibitors is often discussed. Growth in scientific interest in this topic leads to the publication of more and more reports on the metallic NPs used as corrosion inhibitors [28]. These can be used as additions to protective coatings formation via various methods. Moreover, metal and metal oxide are often characterized by high thermal stability and great mechanical properties which makes them useful in different methods of plasma thermal spraying [38] or powder metallurgy techniques [39].

El-Shamy and Deyab [40] have presented a study on biosynthesized AgNPs for epoxy coatings applied on steel substrates for corrosion inhibition in salt environments. Here, *Spirulina platensis* extract was applied for the formation of AgNPs with $AgNO_3$ as a metal precursor. The reaction was carried out by mixing $AgNO_3$ with a prepared extract in a neutral environment (aqueous solution) at RT. Then, the reaction mixture was kept in the dark for 48 hours. Obtained AgNPs were dispersed in epoxy resin and deposited on steel sheet metal rods. For the anticorrosive activity evaluation, coatings were immersed in a 3.5% NaCl solution. The corrosion resistance of the discussed AgNPs-based coating was higher than that of a pure epoxy coating, suggesting that it can be successfully applied for metal protection against saline environments.

The corrosion inhibition ability of AgNPs was also confirmed by Jothi, Balachandran and Palanivelu [41]. In their report, at first, they prepared metallic NPs using *Phyllanthus niruri* leaf extract as a capping agent in the reduction process of $AgNO_3$. Then, the prepared material was incorporated into a sol-gel silane matrix and deposited on stainless steel for the assessment of the anticorrosive abilities of biosynthesized AgNPs in a 3.5% NaCl solution. Coatings enriched with investigated NPS were also compared with unmodified sol-gel films. The authors stated that such a solution was discussed for the first time in the literature. The electrochemical impedance spectroscopy (EIS) studies showed that AgNPs subjected to a silane coating on steel act as excellent corrosion inhibitors. Moreover, the antibacterial assay was performed on *Pseudomonas aeruginosa* and *Escherichia coli* bacteria strains and it was proved that these coatings also have a strong influence on the inhibition of bacteria growth. The presented research shows a successful attempt at the fabrication of protective coatings with the use of green chemistry methods which opens the way for the new field of metallurgy development.

Saha et al. [42] employed a green approach for the sonication, wet-chemical, and hydrothermal synthesis methods of ZnONPs. In this study, ZnONPs were obtained using the reduction of $Zn(OAc)_2$ with the leaf extract of *Psidium guajava*. The resulting powders were then incorporated in chitosan and coated on the cotton fabrics. A comparative assessment of the influence of the processing method of NPs deposited on the cotton fabrics on physicochemical, biological, and photocatalytic properties was prepared. It was shown that NPs produced in a hydrothermal process exhibited the best photocatalytic and antibacterial activity. Moreover, the average particle size of this material was stated at ca. 12 nm. It is believed that the size of NPs is a substantial factor that influences their properties. Consequently, it was shown that ZnONPs not only have a tunable nature (regarding the synthesis method and processing parameters) but also hold great potential for application in functional coatings to impart their protective properties.

Another interesting insight into metal oxide anticorrosive coatings was shown by Sharma and Sharma [43]. The authors attempted to obtain Cr_2O_3NPs using *Cannabis sativa* leaves extract and assess their anticancer and corrosion inhibition activity on mild steel substrates. The weight loss method was applied for the corrosion inhibition activity in HCl, HNO_3, and NH_3 solutions. The highest inhibition performance was observed in an acidic environment. It is worth mentioning, that corrosion inhibition was also influenced by the thermal conditions of measurements. With the increasing temperature, inhibition efficiency decreased, which can be attributed to the desorption of the NPs from the metal surface. Hence, such a solution is limited for application in coatings exposed to high-temperature corrosion. However, green synthesized Cr_2O_3NPs were stated as promising anticorrosive and cytotoxic agents in the application for protective coatings formation.

The work presented by Elizondo-Villarreal et al. [44] aims to synthesize Fe_3O_4 (magnetite) NPs in a single step with the use of green lemon *Citrus aurantifolia* residues extracts. The synthesis was carried out by a co-precipitation method under different temperature conditions. The morphology characterization showed that, depending on the temperature, Fe_3O_4NPs average size was between 3 nm and 12 nm. Next, a composite of magnetite particles and graphene oxide was prepared via an ultrasound-assisted process and applied to ASTM A-662 steel samples for the assessment of their anticorrosive abilities through electrochemical techniques. The coatings showed great anticorrosive properties as well as resistance to abrasion.

4.4. Plant cultivation

The increasing need for the development of agricultural and food processing technologies is mediating environmental pollution. This is caused by the wide usage of fertilizers or pesticides for the enhancement of crop yields. Such substances are often leached to the waterways which have a detrimental impact on the environment. Hence, novel smart fertilizers are willingly developed and the formation of NPs synthesized via plant-based methods can be included in this trend [30]. Although this topic covers different application fields from the ones discussed previously, it is an interesting direction for environmental protection and shows the diversity of green synthesized NPs potential. A brief description of the influence of green synthesized metallic NPs on plant growth and protection against salinity stress is presented below.

Shaikhaldein et al. [45] examined the effects of biosynthesized AgNPs on the antioxidant defense system of *in vitro* raised *Maerua oblongifolia* under different levels of salt stress. AgNPs were synthesized with the *Ochradenus arabicus* extract and $AgNO_3$ by stirring their aqueous solutions at 60°C until the color of the reaction mixture turned dark brown, indicating AgNPs formation. Obtained NPs improved the growth traits and photosynthetic pigment production in investigated plants and caused higher enhancement in antioxidant enzyme activities. It was proved that green synthesized AgNPs augmented the growth of *M. oblongifolia* shoots under saline conditions and it was stated that they can be used as an eco-friendly approach for the enhancement of salinity tolerance in plants.

Mustafa et al. [46] presented an investigation on the toxicological effect of TiO_2NPs synthesized via a green approach with *Buddleja asiatica* L. leaf extract on the morphophysiological properties of wheat plants exposed to salinity stress. NaCl was applied to salinity-tolerant and salinity-susceptible wheat species in different concentrations and after 21 days of germination, TiO_2NPs were applied for the assessment of their influence on salinity stress in plants. After 15 days, a remarkable decrease in morphophysiological attributes of selected wheat species was recorded. Moreover, improvement in plant growth, dry and fresh weight of plants, length of shoots and roots as well as the increase in chlorophyll contents were observed. Such material proved to be a remarkable solution to increase the agronomic and physiological properties of wheat under salinity.

Another article proving the possibility of green synthesized metallic NPs application in agriculture was presented by Mogazy and Hanafy [47]. Here, performed the comparison of the effect of different concentrations of ZnONPs on the growth of faba bean plants under salinity stress. ZnONPs were synthesized using *Mentha spicata* L. plant extract. The response of faba bean plants to the foliar spray of ZnONPs alone and in combination with salt stress was studied. Similarly to previous reports, the treatment of salinity stressed plants with prepared NPs induced an enhancement in plant growth as well as an accumulation of metabolites that help plants overcome the negative effects of salinity.

5. Summary

Green chemistry methods have gained attention as an alternative to conventional chemical techniques for metal and metal oxide NPs production. Reducing or replacing harmful to nature and human health substances used in these processes is crucial to limit their negative impact on the environment. One of the solutions is the use of biosynthesis, in which raw materials of natural origin are used as substrates in the processes of producing NPs.

This article discusses recent advances in the plant-based synthesis of metal and metal oxide NPs. The performed review focuses on discussing the mechanism of green metallic NPs formation and a summary of the most interesting works in this field. Areas of their applications in paints and varnishes formulations with antifouling properties and corrosive inhibitors for functional protective coatings formation were covered. Moreover, a brief description of their use for agricultural and plant cultivation purposes was introduced.

The discussed topic is gaining more and more popularity, mainly because it is based on the use of a green approach to obtaining nanomaterials. Unfortunately, not all of the published to this date works on the plant-based synthesis of NPs are consistent with the green chemistry principles. A critical view on this issue should be pointed out. The authors do not always focus on optimizing the processes of obtaining NPs, and considering how many factors can affect them – they should. Primarily, the preparation of the extracts is vital for the course of the reactions. The following factors are worth mentioning: part of the plant from which the extract is obtained – different parts of the plant contain different content of biocompounds determining metal reduction, and thus may affect the rate and efficiency of the reaction [48]. The changes in the biocompounds concentration in the extract can be also attributed to the pretreatment of the plant. Information about whether the plant was frozen, freeze-dried, or used as fresh raw material is important. Significant differences in the chemical composition of obtained extracts can be observed also depending on the extraction technique used and its conditions. Methods from classic maceration to ultrasound-assisted extraction are commonly used [49].

Apart from the preparation of the extracts, the conditions of the reaction of NPs formation also have a substantial effect on the efficiency of the process and the characteristics of the final product. These include the type of metal precursor and its concentration as well as the molar ratio of applied substrates. In addition, reaction time, temperature, and reaction environment should be taken into account. Currently, among the numerous articles devoted to plant-based metallic NPs formation, only some of them focus on a detailed analysis of the impact of the abovementioned factors on the obtained results. Nevertheless, due to the enormous potential of the green synthesis of metal and metal oxide NPs, the quality of literature reports will continue to improve. This in turn may lead to the gradual implementation of green synthesized nanomaterials in industrial solutions in the near future.

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