Opinion

Catalytic Degradability of \( p \)-Nitrophenol Using Ecofriendly Silver Nanoparticles

Ganesh Shimoga \(^{1,\ast,†} \), Ramasubba Reddy Palem \(^{2,\ast} \), Soo-Hong Lee \(^{2} \) and Sang-Youn Kim \(^{1,\ast} \)

\(^{1} \) Advanced Technology Research Center, Future Convergence Engineering, Korea University of Technology and Education, Cheonan-si 330-708, Chungcheongnam-do, Korea
\(^{2} \) Department of Medical Biotechnology, Dongguk University Biomedical, Campus 32, Goyang-si 10326, Gyeonggi-do, Korea; palemsubbareddy@gmail.com (R.R.P.); soohong@dongguk.edu (S.-H.L.)
\* Correspondence: shimoga@koreatech.ac.kr (G.S.); sykim@koreatech.ac.kr (S.-Y.K.);
Tel.: +82-041-560-1484 (S.-Y.K.)
\† Both authors contributed equally to this work.

Received: 12 November 2020; Accepted: 8 December 2020; Published: 11 December 2020

Abstract: In an effort to produce non-toxic and economically viable “green” protocols for waste water treatment, researchers are actively involved to develop versatile and effective silver nanoparticles (SNPs) as nano-catalyst from bio-based techniques. Since, \( p \)-nitrophenol (PNP) is one of the anthropogenic contaminants, considerable attention has been focused in catalytic degradability of PNP in wastewater treatment by curtailing serious effect on aquatic fauna. Ingestion of contaminants by aquatic organisms will not only affect the aquatic species but is also a potential threat to human health, especially if the toxic contaminants are involved in food chain. In this short report, we provided a comprehensive insight on few remarkable nanocatalysts especially based on SNPs and its biopolymer composites synthesized via ecofriendly “green” route. The beneficaility and catalytic performance of these silver nanocatalysts are concisely documented on standard model degradation reduction of PNP to \( p \)-aminophenol (PAP) in the presence of aqueous sodium borohydride. The catalytic degradation of PNP to PAP using SNPs follows pseudo first order kinetics involving six-electrons with lower activation energy. Furthermore, we provided a list of highly effective, recoverable, and economically viable SNPs, which demonstrated its potential as nanocatalysts by focusing its technical impact in the area of water remediation.

Keywords: anthropogenic; bioreductant; environmental remediation; heterogeneous catalysis; plant extract; \( p \)-nitrophenol; silver nanoparticles

1. Introduction

Organic pollutants from industries are the major source for water pollution; these synthetic toxins are extremely harmful to the environment and influences health risks to human \([1,2]\). Knowledge of the health effects of organic contaminants at the low levels found in industrial wastewater supplies are very limited \([3]\). However, the water source is known to contain significant amounts of industrial effluent and toxic impurities, this has given rise to concern before releasing to the aquatic stream. As anthropogenic contaminants removal from water is essential before domestic use, the cost effectiveness for the water treatment is also to be considered. There is an imperative need to improve the technical knowledge and methods/protocols that should be environmental friendly and anticipated its impact on marine pollution \([4–6]\).

Apart from its immense thermal and electrical conduction, silver metal plays a vital role in catalysis of organic reactions. In recent years, organic reactions in aqueous medium were paid much
attention, so that toxic contaminants can be easily converted into non-hazardous compounds under milder reaction conditions [7–10]. The green synthesized SNPs are effective and have high activity due to large specific surface to volume ratios. In addition, the collective oscillations of delocalized electrons at a metallic surface made the SNPs as efficient catalyst than its bulk counterparts. Since the environmental impact of SNPs on various aquatic organisms are still principally unfamiliar, and the toxic effects of SNPs to organisms is mainly depend on the physicochemical characteristics of nanoparticles [11–13]. It is always beneficial if the SNPs were synthesized via non-hazardous ecofriendly routes rather than using toxic chemicals. In that concern, the various plant extracts were utilized as ecofriendly bioreductants to produce biogenic SNPs. Since the plant extracts possess antiviral, antibacterial, antioxidant, anti-mutagenic, antifungal, and anti-inflammatory properties, they can serve as surface modifiers with unique additional properties for multifunctional performances [14–17]. We can also notice plentiful research reports on the biodegradable polymer and silver nanocomposites, wherein SNPs were prepared in situ on biodegradable polymers and served as heterogeneous catalytic template interfaces for PNP degradation [18–22].

The therapeutic potential of SNPs is mainly dependent on the phytochemicals of the plant extract used in the synthesis. Recently, the chemical stability, biocompatibility, and catalytic activity of SNPs are actively studied along with cytotoxic activities toward cancerous cells with optimal therapeutic concentration [23–25]. The bioreductant from plant origin, especially from the extracts of leaf, gum, root, stem, seed, flower, etc., were used to reduce metal salts. The plant extract containing active phytochemicals such as polyphenols, flavonoids, polysaccharides, catechins, tannic acid, epicatechin gallate, and anthraquinones including rhein and emodin, etc., are responsible for bioreduction of silver salts to achieve stable, controlled size, colloidal polydisperse SNPs. These biogenic SNPs are beneficial due to their reduced regular sizes and possessing practically enhanced antimicrobial properties as well as cytotoxic responses on cancerous cells, which endorse their impact in the field of nanomedicine and nanocatalysis [26–31].

The important factor to consider in pollution remediation process is that employed material should not be another pollutant. In this concern, biodegradable polymers are an exceptional ideal choice for this kind of application [32–34], where metal nanocatalysts based on SNPs produced from plant-mediated ecofriendly routes with/without biopolymers as template materials can effectively serve the purpose. Heretofore, a variety of metal nanoparticles were prepared phyto-chemically and utilized in biomedical and catalytic applications. To the best of our knowledge, there is no concise reports dealing with silver metal based nanocatalysts in combination with unhazardous biopolymer composites for catalytic reduction of PNP [35]. The main objective of this short colloquy is to provide a general overview on the phyto-synthesis of some remarkable functional SNP catalysts and its biopolymer nanocomposites used especially in environmental remediation, for the catalytic degradation of industrial pollutant PNP.

2. Phyto-Synthesis of Silver Nanoparticles and Its Biopolymer Nanocomposites

Besides commensurable to the environmental safety research, development of new nano-technological “green” protocols for the synthesis of metal nanoparticles imparts implementing solution to technical challenges in the field of nanocatalysis [36–39]. The researchers for the reduction of nitroarenes explore varieties of reducing agent, while Fe–HCl is one of the most common reducing agents for nitro compounds reduction. The environmental hazard caused by this Fe–HCl reagent is the massive production of hazardous Fe–FeO sludge with unsatisfactory reaction yields [40–44]. Even though many researchers study SNPs supported variety of templates, plant-mediated green synthesis of SNPs is always a prime choice in environmental remediation. The main advantages of designed nanocatalysts from the plant-mediated “green” route are being inexpensive and specifically providing a controlled size and surface morphology. Another key consideration of plant-mediated SNPs are potent antioxidant, antimicrobial, and cytotoxic activity on cancerous cells in biological systems [45–48]. A systematic study of plant extract mediated synthesis of SNPs with comparative parameters are reported in Table 1.
Recently, a comprehensive review by Iravani [49] highlights the sustainable and eco-friendly synthesis of various nanoparticles along with SNPs of different dimensions using plant gum (an adhesive substance usually obtained as exudate from the tree bark). Since the metal nanoparticles are successfully applied in close proximity of biomedical fields such as pharmaceuticals, tissue engineering, and drug delivery, hazardous toxic substances should be avoided. Concerning this, plant gum polysaccharides plays a vital role with appealing cost effectiveness and biodegradability advantages [50,51]. Thakur et al. and Velusamy et al. reported effective antibacterial SNPs against Bacillus subtilis, Bacillus cereus, Salmonella enteritidis, and Pseudomonas aeruginosa from gums of Acacia Arabica with particle sizes in the range 30.0–35.0 nm [52].

From the aqueous extracts of plant leaves, fruit peels, roots, rhizomes, etc., plentiful research has been undertaken from several decades for the bio-green synthesis of SNPs. The biosynthesized SNPs with sizes 4.0–35.0 nm from Albizia adianthifolia leaves were reportedly effective against A549 lung cell line with viability data of 21% (10 µg/mL) [53]. In contrast, the leaf extract of Alternanthera sessilis Linn. (Amaranthaceae) acts as remarkable capping and reducing agent for silver ions; which shows superior stabilizing behavior with potent antioxidant activities including antimicrobial properties [54]. The SNPs reported by Vivek et al. from Annona squamosa leaf extract were found to be in the range of 20.0 to 100.0 nm and exhibited a dose-dependent cytotoxic effect on human breast cancer cell (MCF-7) with inhibitory concentration (IC50) of 30 µg/mL at 48 h incubation period [55]. The outer peel extract of Ananas comosus (L.) was effective to synthesize antioxidant, antibacterial, and antidiabetic SNPs with cytotoxicity potential towards HepG2 cells [56]. A very fine size of SNPs < 25 nm were reported by Azadirachta indica and Boerhaavia diffusa extracts, which show characteristic surface plasmon resonance of SNPs at around 420.0 nm, and detailed antibacterial assay reveals that these biosynthesized SNPs are active against Gram-positive bacteria Bacillus subtilis and demonstrated highest sensitivity toward Flavobacterium branchiophilum [58,59]. The environmentally amenable SNPs produced from leaf extracts of Brassica oleracea, Caesalpinia pulcherrima, and Cassia auriculata shows potential cytotoxic efficacy towards MCF-7, HeLa, and PC-3 cells, respectively, proves advantageous in biomedical techniques, especially in cancer therapy [60–62]. Balashanmugam et al. reported phytogenically synthesized SNPs from Cassia roxburghii aqueous leaf extract at ambient conditions, showing noteworthy in vitro antifungal activity against human and plant pathogens [63]. Roasted Coffea arabica seed extract facilitated SNPs shows diminished bacterial growth of E. coli and S. aureus [64]. The various cancer cell lines, such as SW480, J-774, MCF-7, MDA-MB-231, HepG2, A549, MCF7, HeLa, SiHa, B16F10, PC3, COLO205, HEP-2, U-87, LoVo, RKO, MDA-MB-231, and HT-29, etc. were studied in detail with varieties of SNPs using phyto-synthetic green routes [65–99]. In combination with biopolymers, these biogenic SNPs are immobilized in the polymer matrix and show greater stability (see Figure 1, for the graphical representation of phyto-synthesis and stability of SNPs in combination with biopolymers); we can also notice superior mechanical and physical properties of biopolymers such as chitosan, agar, and pectin silver nanocomposites [66,77]. The reported biopolymer based silver nanocomposite films shows potential applications in food packaging [77,90–92].
Table 1. Partial list of comparative parameters reported for plant extract mediated synthesis of SNPs.

| Name of Plant              | Source       | Size of Silver Nanoparticles (SNPs) (nm) | Ultraviolet-Visible Spectroscopy (UV-Vis) RANGE (nm) | Antimicrobial Activity          | Cytotoxicity Effective on          | References  |
|----------------------------|--------------|------------------------------------------|------------------------------------------------------|-------------------------------|-----------------------------------|-------------|
| Acacia arabica             | Gum          | 35.0                                     | 435.0                                                | Effective                      | NR                                | [52]        |
| Albizia adianthifolia      | Leaves       | 4.0–35.0                                 | 448.0                                                | Effective                      | NR                                | [53]        |
| Alternanthera sessilis Linn. | Leaves     | 20.0–30.0                                | 435.0                                                | Effective                      | NR                                | [54]        |
| Ananas comosus L.          | Peels        | NR                                       | 485.0                                                | Effective                      | HepG2 cells                       | [55]        |
| Annona squamosa            | Leaves       | 20.0–100.0                               | 444.0                                                | NR                             | MCF-7 cells                       | [56]        |
| Azadirachta indica L.      | Gum          | <35.0                                    | 418.0                                                | Effective                      | NR                                | [57]        |
| Azadirachta indica         | Leaves       | 11.5                                     | 421.0                                                | Effective                      | NR                                | [58]        |
| Boerhaavia diffusa         | Plant        | 25.0                                     | 418.0                                                | Effective                      | NR                                | [59]        |
| Brassica oleracea          | Leaves       | 20.0                                     | 415.0                                                | Effective                      | MCF-7 cell                        | [60]        |
| Caesalpinia pulcherrima     | Leaves       | 410.0                                    | 410.0                                                | Effective                      | HeLa cell                         | [61]        |
| Cassia auriculata          | Leaves       | 30.0–50.0                                | 423.0                                                | Effective                      | PC-3 cell                         | [62]        |
| Cassia roxburghii          | Leaves       | 10.0–30.0                                | 435.0                                                | Effective                      | NR                                | [63]        |
| Coffea arabica             | Seeds        | 20.0–30.0                                | 445.0–459.0                                          | Effective                      | SW40 cells                        | [64]        |
| Commiphora myrrha          | Plant        | 0.5–25.0                                 | 445.0                                                | Effective                      | NR                                | [65]        |
| Coptis Chinensis + Chitosan | Rhizome     | 15.0–20.0                                | 428.0                                                | Effective                      | J-774 cell                        | [66]        |
| Cucumis prophetarum        | Leaves       | 30.0–50.0                                | 420.0                                                | Effective                      | MCF-7, MDA-MB-231, Hepg2, & A549 | [67]        |
| Datura inoxia              | Leaves       | 13.0–60.0                                | 420.0                                                | Effective                      | MCF-7 cells                       | [68]        |
| Delphinium denudatum       | Roots        | <85.0                                    | 416.0                                                | Effective                      | Aedes aegypti                     | [69]        |
| Diospyros lotus            | Leaves       | 20.0                                     | 409.0                                                | Effective                      | NR                                | [70]        |
| Emblica officinalis        | Fruits       | 10.0–70.0                                | 432.0–436.0                                          | Effective                      | NR                                | [71]        |
| Erythrina indica lam       | Roots        | 20.0–118.0                               | 438.0                                                | Effective                      | MCF-7 & HEPG2 cell                | [72]        |
| Ginkgo biloba              | Leaves       | 8.0–21.0                                 | 400.0–413.0                                          | Effective                      | NR                                | [73]        |
| Ginkgo biloba              | Leaves       | 20.0–90.0                                | 448.0                                                | NR                             | HeLa, and SiHa                    | [74]        |
| Grewia flaviscences        | Leaves       | 60.0                                     | 380.0–460.0                                          | Effective                      | NR                                | [75]        |
| Indigofera hirsuta L.      | Leaves       | 5.0–10.0                                 | 436.0                                                | Effective                      | B16F10, PC3 & COLO205             | [76]        |
| Lagerstroemia speciose + Agar | Fruits    | 32.0–62.0                                | 412.0                                                | Effective                      | NR                                | [77]        |
| Limonia acidissima         | Leaves       | <30.0                                    | 425.0                                                | Effective                      | NR                                | [78]        |
| Malus domestica            | Apples       | 20.0                                     | 420.0                                                | Effective                      | MCF-7                            | [79]        |
| Manilkara zapota           | Leaves       | 70.0–140.0                               | 421.0                                                | NR                             | Anopheles subpictus               | [80]        |
| Melia azedarach            | Leaves       | 78.0                                     | 436.0                                                | NR                             | HeLa                             | [81]        |
| Morinda citrifolia         | Roots        | 32.0–55.0                                | 413.0                                                | NR                             | HeLa                             | [82]        |
Table 1. Cont.

| Name of Plant                  | Source          | Size of Silver Nanoparticles (SNPs) (nm) | Ultraviolet-Visible Spectroscopy (UV-Vis) RANGE (nm) | Antimicrobial Activity | Cytotoxicity Effective on | References |
|--------------------------------|-----------------|----------------------------------------|-----------------------------------------------|------------------------|---------------------------|------------|
| Origanum vulgare               | Leaves          | 136.0                                  | 440.0                                         | NR                     | A549 cell                 | [83]       |
| Phoenix dactylifera, Ferula asaefida, Acacia nilotica | Fruits          | 67.0–156.0                             | 420.0–440.0                                   | Effective              | LoVo                      | [84]       |
| Piper longum                   | Leaves          | 17.6–41.0                              | 420.0                                         | NR                     | HEp-2 cell                | [85]       |
| Plectranthus amboinicus        | Leaves          | 18.0                                   | 428.0                                         | Effective              | NR                        | [86]       |
| Potentilla fulgens             | Roots           | 10.0–15.0                              | 400.0–450.0                                   | Effective              | MCF-7 & U-87              | [87]       |
| Prosopis juliflora             | Leaves          | 11.0–19.0                              | 420.0                                         | Effective              | NR                        | [88]       |
| Punica granatum                | Peels           | 20.0–40.0                              | 378.0                                         | Effective              | RKO cells                 | [89]       |
| Rheum rhabarbarum              | Stems           | 60.0–80.0                              | 420.0–460.0                                   | Effective              | HeLa                      | [90]       |
| Rheum rhabarbarum + Chitosan   | Stems           | 50.0                                   | 433.0                                         | Effective              | HeLa                      | [91]       |
| Ribes nigrum                   | Fruits          | 5.0–10.0                               | 450.0                                         | Effective              | A549 cells                | [92]       |
| Rosmarinus officinalis         | Leaves          | 12.0–22.0                              | 400.0                                         | Effective              | MDA MB 231                | [93]       |
| Sapindus mukorossi             | Extract         | 35.0                                   | 420.0                                         | Effective              | NR                        | [94]       |
| Sargassum polycystum           |                 | 28.0                                   | 405.0                                         | Effective              | HT-29 cells               | [95]       |
| Solanum trilobatum             | Fruits          | 12.0–41.0                              | 432.0                                         | Effective              | MCF 7                     | [96]       |
| Syzygium aromaticum            | Cloves          | 5.0–40.0                               | 441.0                                         | NR                     | MCF 7 & A549              | [97]       |
| Terminalia chebula             | Leaves          | 10.0–30.0                              | 421.0                                         | Effective              | NR                        | [98]       |

NR = Not reported.
Additionally, the synthesized SNPs are stabilized by functional groups of phytochemicals present in the plant extract. We can notice plentiful research on phyto-synthesis of various nanomaterials, such as gold, platinum, copper, gold, titanium, and zinc, etc., but SNPs have proved their efficiency as a potent antimicrobial agent with unique optical, electrical, thermal, and catalytic properties [103,104]. The increasing popularity of phyto-synthesis, the so-called “green route” for SNPs offer many advantages over routine chemical synthesis. Plant extracts (from leaf, gum, roots, stems, rhizomes, seeds, flowers etc.) have a rich source of active phytochemicals such as catechins, anthraquinones, phenolics, terpenoids, flavonoids, tannins, enzymes, proteins, polysaccharides, and organic acids, etc. These biomolecules took active part in the complex mechanism of reduction and stabilization of SNPs from silver ions [105,106]. (See Figure 1 for phyto-synthesis and stability of SNPs).

3. Catalytic Degradation of p-Nitrophenol Using Silver Nanoparticles

The presence of the various functional entities such as amine, hydroxyl, carbonyl and carboxyl groups with carbohydrate polymer frameworks are responsible for the synthesis of SNPs by bioreduction process [100,101]. Some researchers synthesized SNPs successfully using cyanobacterium algae [102]. Additionally, the synthesized SNPs are stabilized by functional groups of phytochemicals present in the plant extract. We can notice plentiful research on phyto-synthesis of various nanomaterials, such as gold, platinum, copper, gold, titanium, and zinc, etc., but SNPs have proved their efficiency as a potent antimicrobial agent with unique optical, electrical, thermal, and catalytic properties [103,104]. The increasing popularity of phyto-synthesis, the so-called “green route” for SNPs offer many advantages over routine chemical synthesis. Plant extracts (from leaf, gum, roots, stems, rhizomes, seeds, flowers etc.) have a rich source of active phytochemicals such as catechins, anthraquinones, phenolics, terpenoids, flavonoids, tannins, enzymes, proteins, polysaccharides, and organic acids, etc. These biomolecules took active part in the complex mechanism of reduction and stabilization of SNPs from silver ions [105,106]. (See Figure 1 for phyto-synthesis and stability of SNPs).

The extent of toxic compounds impact on the environment leads to a significant effect on exposed organisms. We can encounter the aggregation of the toxic components in the natural environment especially to air, soil, and water. The environmental pollution is a serious problem and has a devastating effect on nature because of the chain of events that ensue the toxic contaminants and eventually enter into the natural environment [107,108]. In spite of other sources of pollution, industries are the worst generators of toxic contaminants. The contaminants finally enters the environment and sequentially contaminate water by degrading the water quality, rendering toxicity to aquatic life and humans [109–111]. The major effluent from pesticides, explosives, and dye industries are nitrophenols; these toxic organic anthropogenic pollutants can easily enter into the aquatic stream if the appropriate precautionary measures are not implemented on effluent treatment. Due to the remarkable demonstration and significant catalytic activity of SNPs, many researchers documented the efficient catalytic degradation of nitroarenes from industrial wastewater [112–118]. The main criteria of the developed nanocatalyst are environmentally friendly, economically viable, biodegradable, and non-toxic with multifunctional behavior such as high adsorption, removal ability, and reusability.

We can find plentiful applications of sodium borohydride in various catalytic reactions. The use of sodium borohydride as a reducing agent is reported in various organic and inorganic reactions [119–121]. In contrast, the reduction of PNP is not possible by sodium borohydride alone. The ratio of potential difference for PNP to PAN is −0.76 V and H₃BO₃/ BH₄⁻ is −1.33 V at ambient temperature. Even though the reaction of PNP to PAP is thermodynamically favorable, the conversion reaction is kinetically too slow [122]. This is due to the presence of kinetic barrier and potential difference between borohydride (donor) to p-nitrophenolate ions (acceptor). The SNPs overcome this kinetic barrier by catalyzing the
reaction and facilitating the relay of electrons from the donor to acceptor molecules. The interaction of aqueous sodium borohydride with SNPs quickly generates hydrogen gas and adsorb on the SNPs surface, which further enables the reduction process by interactive adsorption of \( p \)-nitrophenolate ions on the SNPs surface [123]. The reaction involves various organic intermediates and finally desorption of \( p \)-aminophenolate ions from the SNPs surface (for graphical representations, see Figure 2). In accordance with the catalyst, the analyte PNP in presence of sodium borohydride follows pseudo-first-order kinetics [124,125]. The electron transfer reaction from borohydride ions to \( p \)-nitrophenolate ions will transpire after the adsorption of donor-acceptor molecules on SNPs surface. The reaction proceeds by diminishing the activation energy and SNPs catalyst play a vital role in the catalytic reaction (For graphical representations, see Figure 3). It is believed that the conversion of PNP to PAP is a six-electron transfer reaction in the presence of sodium borohydride; the conviction was also supported by the reaction intermediates isolated and studied via mass-spectrometric techniques [126,127] (see Figure 4).

**Figure 2.** Phyto-synthesis of SNPs and catalytic reduction of \( p \)-nitrophenol (PNP) on SNPs surface in presence of sodium borohydride.

**Figure 3.** Graphical representation of activation energy and catalytic reduction of PNP to \( p \)-aminophenol (PAP).
For brief understanding, the reduction of PNP is not possible by using sodium borohydride alone. After adding SNPs catalyst to PNP in presence of aqueous sodium borohydride, the formed \( p \)-nitrophenolate shows the maximum absorption (\( \lambda_{\text{max}} \)) in UV–vis spectrum in the range of 400–410 nm. The time dependent UV–vis spectrum is to be recorded to check the progress of the catalytic reaction. The diminishing peak of \( \lambda_{\text{max}} = 400–410 \text{ nm} \) was observed with the appearance of new \( \lambda_{\text{max}} \) peak at around 300–320 nm, which is due to the formation of \( p \)-aminophenolate ions in the reaction mixture. Further, decrease in the pH of the solution was observed due to the addition of sodium borohydride, which enables the conversion of PNP to PAP [127,129]. The use of sodium borohydride concentration is significantly higher than the concentration of PAP, and the reduction rates are independent of the sodium borohydride concentration, accordingly the reaction follows the pseudo-first order reaction [130,131], the equation can be written as follows:

\[
-k_1 S = -k_{\text{app}} t = \ln \frac{C_t}{C_0}
\]

where \( k_{\text{app}} \) (\( k_1 S \) according to Langmuir–Hinshelwood mechanism) is the apparent rate constant; \( t \) is the reaction time; \( C_0 \) is the relative concentration of PNP at time zero (initial concentration); \( C_t \) is the concentration of the PNP at time ‘\( t \)’ (different interval of time during the catalytic reaction). From this equation, it is obvious that the higher the value of apparent rate constant (\( k_{\text{app}} \)) for the catalytic reaction, the more efficient is the used catalyst [132,133].

Various researchers investigated the catalytic efficacy of ecofriendly SNPs prepared from several plants of different source. The comprehensive list was reported in Table 2. These effective SNPs catalysts show remarkable catalytic degradation efficiency against PNP, one of the main mutagenic organic pollutants. Researchers successfully carried out catalytic reactions by removing PNP in aqueous media using biogenic SNPs. The obtained SNPs are spectro-chemically characterized using different advanced analytical techniques such as Ultraviolet-Visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX), dynamic light scattering (DLS), and X-ray photoelectron microscopy (XPS), etc.

Previously, we reported the biosynthesis of SNPs from Rhubarb stem extract (RS extract) as bioreductant. In brief, the chopped Rhubarb stems were suspended in hot double distilled water for about 1 h and filtrate was collected and stored under \(<5^\circ \text{C} \) for further use. The RS extract was mixed stoichiometrically with silver nitrate solution at different interval of time to get ecofriendly SNPs [designated here as RS-AgNPs (Rhubarb stem extract—Silver nanoparticles)] within 15 min. The RS extract was lyophilized to get in powder form to compare the morphology with RS-AgNPs [91].
Table 2. Partial list of catalytic reduction reaction parameters of PNP to PAP reported for ecofriendly SNPs in the literature.

| Prepared SNPs Catalyst from Plant Source | SNPs Size (nm) | Catalyst Loading | Conversion Time (min) | PNP (mM) | BH₄⁻ (mM) | Rate Constant ($k_{app}$) | References |
|------------------------------------------|----------------|-----------------|----------------------|----------|-----------|--------------------------|------------|
| *Acacia nilotica* (Gum)                 | 10.0–40.0      | a 1.5 mg        | 12.0                 | 4.3      | 100.0     | 0.3606 min⁻¹             | [134]      |
| *Acacia nilotica* (Stem)                | <50.0          | 5.0 mg          | 10.0                 | 0.1      | 0.1       | 0.0806 min⁻¹             | [135]      |
| *Actinodaphne madraspatana* (Leaves)    | <60.0          | 5.0 mg          | 1.5                  | 1.0      | 5.0       | 13.25 × 10⁻³ s⁻¹         | [127]      |
| *Aglaia elaeagnoidea* (Flowers)         | 17.0           | NR              | 15.0                 | 0.1      | 10.0      | 22.5 × 10⁻² min⁻¹        | [136]      |
| *Aglia elaeagnoidea* (Leaves) + Alginate| 12.0           | 144.8 mg        | 5.0                  | 1.0      | 10.0      | 0.5054 min⁻¹             | [137]      |
| *Allium ampeloprasum L.* (Leaves)       | 2.0–43.0       | NR              | 12.0                 | 20.0     | 500.0     | 0.2596 min⁻¹             | [138]      |
| *Arctium lappa* (Roots)                 | 21.3           | 1.0 mg          | 12.0                 | 0.1      | 1000.0    | 6.77 × 10⁻² s⁻¹          | [139]      |
| *Bryonia alba* (Leaves)                 | <20.0          | 5.0 mg          | ≈30.0 b              | 2.5      | 250.0     | NR                       | [140]      |
| *Caulerpa serrulata* (Green Algae)      | 10.0           | 0.1 mL          | 5.0                  | NR       | 1.74      | 0.580 min⁻¹              | [141]      |
| *Centella asiatica* (Aerial Parts)      | 20.0–25.0      | NR              | 21.5                 | 21.5     | 3.9 × 10⁻³ s⁻¹         | [142]      |
| *Cicer arietinum* (Leaves)              | 88.8           | 40.0 mg         | 2.0                  | NR       | 30.0      | NR                       | [143]      |
| *Cicorium intybus L.* (Leaves) + Pistachio shell | 10.0–15.0 | 5.0 mg          | 0.51                 | 2.5      | 250.0     | NR                       | [144]      |
| *Coleus forskohlii* (Roots)             | 35.0–55.0      | 25.0 µL         | 24.0                 | 50.0     | 0.10118 min⁻¹        | [145]      |
| *Colocasia esculenta* (Rhizome)         | 68.0           | 3.3 mg          | 6.0                  | 1.0      | 500.0     | 5.27 × 10⁻³ s⁻¹          | [128]      |
| *Cyperus Rotundus* (Rhizome)            | 10.0–40.0      | 100.0 µL        | 1.0                  | 100.0    | 0.293 min⁻¹         | [146]      |
| *Dalbergia spinosa* (Leaves)            | 18.0           | 200.0 µL        | 40.0                 | 0.1      | 10.0      | 0.2596 min⁻¹             | [147]      |
| *Ginger* (Rhizome)                     | 25.0           | 2.8 mg          | 14.0                 | 1.0      | 1.0       | 2.38 × 10⁻³ s⁻¹          | [148]      |
| *Ginkgo biloba* (Leaves)                | 20.0–40.0      | 0.2 mg          | 100.0                | 2.5      | 250.0     | 0.0452 min⁻¹             | [149]      |
| *Hamamelis virginiana* (Leaves)        | 8.0–25.0       | 0.24 mg         | 4.0                  | 2.5      | 250.0     | NR                       | [150]      |
| *Lavandula angustifolia* (Leaves)       | 18.0           | 0.2 µL          | 15.0                 | 1.0      | 1.0       | NR                       | [151]      |
| *Phaseolus vulgaris* (Beans)            | 10.0–20.0      | 1590.0 mM       | 15.0                 | 50.0     | 200.0     | 1.59 mM/g/h              | [152]      |
| *Punica granatum* (Peels)               | 30.0           | 10.0 µL         | NR                   | 1.0      | 1.0 mg c | NR                       | [153]      |
| *Punica granatum* (Seeds)               | 10.0–35.0      | 50.0 µL         | 7.0                  | 5.0      | 1000.0    | 0.1424 min⁻¹             | [154]      |
| *Rheum rhabarbarum* (Stems) + Guar gum  | <10.0          | 100.0 mg        | 14.0                 | 0.6      | 100.0     | 0.1218 min⁻¹             | [155]      |
| *Rubus crataegifolius* (Bge Fruits)     | 13.0           | 100.0 µL        | 30.0                 | 0.1      | 5.0       | NR                       | [156]      |
| *Simarouba glauca* (Leaves)             | 7.0            | 0.01 mg         | 6.0                  | 0.1      | 10.0      | 18.424 × 10⁻³ s⁻¹        | [157]      |
| *Stachys Lavandulifolia* + MWCNT         | 3.15           | 0.06 mg         | 4.0                  | 0.2      | 150.0     | 1.92 × 10⁻² s⁻¹          | [158]      |
| *Syzygium aromaticum* (Clove)           | 9.0            | 5.0 mg          | 30.0                 | NR       | 100.0     | 0.07494 min⁻¹            | [159]      |
| *Terminalia bellerica kernel* (Fruits)   | 29.6           | 0.4 mg          | 60.0                 | 0.001    | 500.0     | 0.03 min⁻¹               | [160]      |
| *Thymbra spicata* (Leaves)              | 7.0            | 0.35 mg         | 1.0                  | 0.002    | 250.0     | 0.0645 s⁻¹               | [161]      |
| *Tulsi* (Leaves)                        | 5.0–10.0       | 10.0 µL         | 30.0                 | 5.0      | 200.0     | 2.048 min⁻¹              | [162]      |
| *Ziziphus spina-christi* (Leaves)       | 15.0           | 50.0 µL         | 15.0                 | 10.0     | 100.0     | 4.4 × 10⁻³ s⁻¹           | [163]      |

NR = Not reported, a 1.5 mg mL⁻¹ of SNPs, b Not completely converted, c 1 mg of sodium borohydride in 1.5 mL of 1 mM SNPs solution.
It is evident from the Figure 5 that, we can easily distinguish RS extract powder with RS-AgNPs, the adopted synthetic process does not involve any harmful chemicals. The morphology of RS-AgNPs demonstrate SNPs capped with various phytochemical groups of RS extract. Recently, by varying the amount of guar gum biopolymer, we formulated biopolymer silver nanocomposites (designated here as AgNC@PAAG1). The developed silver nanocomposites demonstrate its efficacy against model reduction reaction of PNP to PAP by aqueous sodium borohydride with apparent rate constant of $121.8 \times 10^{-3} \text{ min}^{-1}$ at ambient temperature. In addition, silver nanocomposite hydrogels prepared from RS extract showed potent antimicrobial activity against *B. subtilis* and *E. coli*. We also proposed drug delivery application of these silver nanocomposite hydrogels [155]. The morphology of developed guar gum based silver nanocomposite hydrogels are portrayed in Figure 6, which signpost uniform distribution of SNPs throughout the hydrogel networks.

![Figure 5](image1.png)

**Figure 5.** (a) Synthesis of RS-AgNPs from *Rhubarb* stem extract (RS extract), (b) Pictograph and SEM morphology of RS extract and RS-AgNPs. Adopted from [91], with permission from Springer, 2018.

![Figure 6](image2.png)

**Figure 6.** SEM morphology of guar gum based silver nanocomposite hydrogels (a) surface view of AgNC@PAAG1 (b) cross-sectional view of AgNC@PAAG1. (Scale = 100 µm, 10 µm and 500 nm, respectively, from left to right). Adopted from [155], with permission from Elsevier, 2020.

Gavade et al. synthesized biogenic SNPs catalyst from *Acacia nilotica* gums and its catalytic efficiency towards PNP was reported with different catalytic quantities, the catalytic loading of 15.0 mg·mL$^{-1}$ of SNPs shows better performances in converting PNP to PAP within 12.0 min with $k_{app}$ value 0.03651 min$^{-1}$ [134]. In contrast, SNPs synthesized form stem extracts of *Acacia nilotica* shows comparatively higher catalytic efficiency, if we consider the concentration of sodium borohydride
used in the reaction [135]. Using *Actinodaphne madraspatana* bedd leaves, Priya et al. synthesized and reported the size dependent catalytic activity of SNPs. The SNPs of different sizes (60, 35, and 20 nm) were prepared at different pH (6.0, 9.0, and 12.0), respectively. The authors noticed the catalytic activity, it was found to increase with decrease in SNPs size. For the SNPs size of ≈20.0 nm, authors testified significant $k_{app}$ value of $13.25 \times 10^{-3}$ s$^{-1}$ with conversion time within 1.5 min [127]. Manjari et al. documented the facile synthesis of SNPs using *Aglaia elaeagnoida* flower extract. The authors mentioned the conversion time of PNP to PAP is around 15.0 with $k_{app}$ value $22.5 \times 10^{-2}$ min$^{-1}$ [136]. In contrast, the leaf extract of *Aglaia elaeagnoida* produce average 12.0 nm size SNPs inside the sodium alginate gel network and shows extraordinary conversion efficiency. The prepared SNPs incorporated alginate gel beads shows superior catalytic recyclability up to 10.0 consecutive cycles with ≈80% conversion efficacy. The authors claim that the minimum loss of catalyst (<4%) was observed during the course of catalytic reaction throughout 10 successive cycles [137].

The SNPs prepared form different sources (leaves, roots, rhizome, peels, seeds, cloves, fruits, beans) plants were reported in Table 2 with various parameters including $k_{app}$ values [138–154,156–161,163]. Recently, we reported guar gum-silver nanocomposite hydrogels using *rhubarb* stem-extract as bioreductant. These SNP's gels shows remarkable $k_{app}$ value 0.1218 min$^{-1}$ with higher recyclable efficiency [154]. The comprehensive list reported in Table 2 also includes SNPs prepared from medicinal plants like Ginger rhizomes and *Tulsi* leaves, which shows $k_{app}$ values of $2.38 \times 10^{-3}$ s$^{-1}$ and 2.048 min$^{-1}$, respectively [148,162].

4. Conclusive Remarks

Currently, our ecosystem is becoming extremely unpleasant due to the release of anthropogenic pollutants from different industries to the environment. Due to this, pollutants are contaminating our natural water resources across the world. To interpret the experimental kinetic data of an organic pollutant, PNP from industrial wastewater, it is reasonable to utilize these phytochemical-induced, unhazardous SNPs and its biopolymer conjugates in catalytic processes. These biogenic SNPs demonstrate advantageous surface chemistry, because these SNPs are stabilized by phytochemical functional groups. It was noticed that, they exhibit remarkable antimicrobial properties and potent cytotoxic responses on cancerous cells.

In line with several benefits of “green” SNPs and its biopolymer composites, various functional parameters—particularly surface area and porosities of SNPs incorporated gel networks—are also to be expected for the favorable catalytic activity, which can enhance the interaction between the supported biopolymer templates and SNPs, and predict apparent rate constant ($k_{app}$) of the nanocatalysts. Despite this, the nature of phyto-synthesized SNPs and its biopolymer composite materials have been extensively studied along with some congruent reports. A number of advantageous points have been agreed upon as follows:

- A series of well-stabilized SNPs can be achieved with tunable size distribution using plant-mediated protocols.
- Biodegradable and non-toxic polymers in combination with ecofriendly SNPs always play an important role in medicinal and food-based industries.
- Chemical synthesis of SNPs involve the usage of toxic reducing agents and are the subject of environmental concern, so it should be avoided.
- Dynamic tunability of antimicrobial activity of plant-mediated SNPs toward various bacterial strains and several human viral pathogens were observed.
- Ecofriendly SNPs demonstrate extraordinary and unique optical, thermal, and electrical properties of SNPs attracted researchers to utilize in diverse technical fields from photovoltaics to chemical sensors.
• Fabrication of ecofriendly SNPs and its non-toxic biopolymer composites with multi-functional properties are owing to superior catalytic degradability of PNP and wide range of applications in nanocatalysis.

Author Contributions: Both authors, G.S. and R.R.P. contributed equally to write the article; S.-H.L. contributed in final editing of the manuscript; S.-Y.K. supervised and approved the final manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Research Foundation of Korea (NRF) grant funded by Ministry of Education (NRF-2020R1I1A3065371). The work was also supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2018R1A6A1A03025526).

Acknowledgments: We acknowledge Cooperative Equipment Center at KoreaTech for formal discussions and the authors G.S. and R.R.P. respectively acknowledge KoreaTech and Dongguk University for providing the opportunity and research facilities.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Carpenter, D.O. Health effects of persistent organic pollutants: The challenge for the Pacific Basin and for the world. Rev. Environ. Health 2011, 26, 61–69. [CrossRef] [PubMed]
2. Ruzzin, J. Public health concern behind the exposure to persistent organic pollutants and the risk of metabolic diseases. BMC Public Health 2012, 12, 298. [CrossRef] [PubMed]
3. United States Environmental Protection Agency. Persistent Organic Pollutants: A Global Issue, a Global Response. Available online: https://www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-response (accessed on 10 November 2020).
4. Bedding, N.D.; McIntyre, A.E.; Perry, R.; Lester, J.N. Organic contaminants in the aquatic environment I. Sources and occurrence. Sci. Total Environ. 1982, 25, 143–167. [CrossRef]
5. Hjeresen, D.J.; Alamos, L. Green Chemistry: The impact on water quality and supplies (Chapter 2). In Water and Sustainable Development—Opportunities for the Chemical Sciences (A Workshop Report to the Chemical Sciences Roundtable); Norling, P., Wood-Black, F., Masciangioli, T.M., Eds.; The National Academies Press: Washington, DC, USA, 2004; ISBN 0-309-09200-0.
6. Royal Society of Chemistry. Silver. Available online: https://www.rsc.org/periodic-table/element/47/silver#:~!:text=Silver%20is%20used%20to%20make,used%20for%20making%20printed%20circuits (accessed on 10 November 2020).
7. Geology News and Information. The Many Uses of Silver. Available online: https://geology.com/articles/uses-of-silver/ (accessed on 10 November 2020).
8. Lo, V.K.-Y.; Chan, A.O.-Y.; Che, C.-M. Gold and silver catalysis: From organic transformation to bioconjugation. Org. Biomol. Chem. 2015, 13, 6667–6680. [CrossRef] [PubMed]
9. Mudarra, A.L.; de Salinas, S.M.; Pérez-Temprano, M.H. Beyond the traditional roles of Ag in catalysis: The transmetalating ability of organosilver(i) species in Pd-catalysed reactions. Org. Biomol. Chem. 2019, 17, 1655–1667. [CrossRef] [PubMed]
10. Ahmad, S.; Munir, S.; Zeb, N.; Ullah, A.; Khan, B.; Ali, J.; Bilal, M.; Omer, M.; Alamzeb, M.; Salman, S.M.; et al. Green nanotechnology: A review on green synthesis of silver nanoparticles—An ecofriendly approach. Int. J. Nanomed. 2019, 14, 5087–5107. [CrossRef]
16. Rafique, M.; Sadaf, I.; Rafique, M.S.; Tahir, M.B. A review on green synthesis of silver nanoparticles and their applications. *Artif. Cells Nanomed. Biotechnol.* 2017, 45, 1272–1291. [CrossRef] [PubMed]

17. Siddiqi, K.S.; Husen, A.; Rao, R.A.K. A review on biosynthesis of silver nanoparticles and their biocidal properties. *J. Nanobiotechnol.* 2018, 16, 14. [CrossRef] [PubMed]

18. Mahiuddin, M.; Saha, P.; Ochiai, B. Green Synthesis and Catalytic Activity of Silver Nanoparticles Based on *Piper chaba* Stem Extracts. *Nanomaterials* 2020, 10, 1777. [CrossRef]

19. Gangula, A.; Podila, R.; Ramakrishna, M.; Karanam, L.; Janardhana, C.; Rao, A.M. Catalytic Reduction of 4-Nitrophenol using Biogenic Gold and Silver Nanoparticles Derived from *Breynia hamnoides*. *Langmuir* 2011, 27, 15268–15274. [CrossRef]

20. Capeness, M.; Echavarri-Bravo, V.; Horsfall, L.E. Production of Biogenic Nanoparticles for the Reduction of 4-Nitrophenol and Oxidative Laccase-Like Reactions. *Front. Microbiol.* 2019, 10, 997. [CrossRef]

21. Burlacu, E.; Tanase, C.; Coman, N.-A.; Berta, L. A Review of Bark-Extract-Mediated Green Synthesis of Metallic Nanoparticles and Their Applications. *Molecules* 2019, 24, 4354. [CrossRef]

22. Park, Y. A New Paradigm Shift for the Green Synthesis of Antibacterial Silver Nanoparticles Utilizing Plant Extracts. *Toxicol. Res.* 2014, 30, 169–178. [CrossRef]

23. Kulandaivelu, B.; Gothandam, K.M. Cytotoxic Effect on Cancerous Cell Lines by Biologically Synthesized Silver Nanoparticles. *Braz. Arch. Biol. Technol.* 2016, 59, e16150529. [CrossRef]

24. Suganya, S.; Dhanalakshmi, B.; Kumar, S.D.; Santhanam, P. Cytotoxic Effect of Silver Nanoparticles Synthesized from *Sargassum triangularis* on Cervical Cancer Cell Line. *Proc. Natl. Acad. Sci. USA India Sect. B Biol. Sci.* 2020, 90, 811–818. [CrossRef]

25. Selvi, B.C.G.; Madhavan, J.; Santhanam, A. Cytotoxic effect of silver nanoparticles synthesized from Padina tetrastromatica on breast cancer cell line. *Adv. Nat. Sci. Nanosci. Nanotechnol.* 2016, 7, 035015. [CrossRef]

26. Stephen, A.; Seethalakshmi, S. Phytochemical Synthesis and Preliminary Characterization of Silver Nanoparticles Using Hesperidin. *J. Nanosci.* 2013, 2013, 126564. [CrossRef]

27. Nurchin, F.; Larijani, K.; Rustaiyan, A.; Ebrahimi, S.N.; Tafvizi, F. Phytochemical Synthesis of Silver Nanoparticles by Two Techniques Using *Saturaja rechgr* Jamzad Extract: Identifying and Comparing *in Vitro* Anti-Proliferative Activities. *Adv. Pharm. Bull.* 2018, 8, 235–244. [CrossRef] [PubMed]

28. Azizian-Shermeh, O.; Valizadeh, M.; Taherizadeh, M.; Beigomi, M. Phytochemical investigation and phytosynthesis of eco-friendly stable bioactive gold and silver nanoparticles using petal extract of saffron (*Crocus sativus* L.) and study of their antimicrobial activities. *Appl. Nanosci.* 2020, 10, 2907–2920. [CrossRef]

29. Ratan, Z.A.; Haidere, M.F.; Nurunnabi, M.; Shahriar, S.M.; Shahriar, A.J.S.; Shim, Y.Y.; Reaney, M.J.T.; Cho, J.Y. Green Chemistry Synthesis of Silver Nanoparticles and Their Potential Anticancer Effects. *Cancers* 2020, 12, 855. [CrossRef] [PubMed]

30. Mallikarjuna, K.; Sushma, N.J.; Narasimha, G.; Manoj, L.; Raju, B.D.P. Phytochemical fabrication and characterization of silver nanoparticles by using *Pepper* leaf broth. *Arab. J. Chem.* 2014, 7, 1099–1103. [CrossRef]

31. Khorrami, S.; Khorrami, A.; Khorrami, A. Green synthesis of silver nanoparticles at low temperature in a fast pace with unique DPPH radical scavenging and selective cytotoxicity against MCF-7 and BT-20 tumor cell lines. *Biotecnol. Rep.* 2019, 24, e00393. [CrossRef]

32. Kim, J.; Kwon, S.; Jeong, S. Preparation of biodegradable polymer/silver nanoparticles composite and its antibacterial efficacy. *J. Nanosci. Nanotechnol.* 2009, 9, 1098–1102. [CrossRef]

33. Krasniewska, K.; Galus, S.; Gniewosz, M. Biopolymers-Based Materials Containing Silver Nanoparticles as Active Packaging for Food Applications—A Review. *Int. J. Mol. Sci.* 2020, 21, 698. [CrossRef]

34. Carbone, M.; Donia, D.M.; Sabbatella, G.; Antiochia, R. Silver nanoparticles in polymeric matrices for fresh food packaging. *J. King Saud Univ. Sci.* 2016, 28, 273–279. [CrossRef]

35. Safari, J.; Najafabadi, A.E.; Zamegar, Z.; Masoule, S.F. Catalytic performance in 4-nitrophenol reduction by Ag nanoparticles stabilized on biodegradable amphiphilic copolymers. *Green Chem. Lett. Rev.* 2016, 9, 20–26. [CrossRef]

36. Rodrigues, T.S.; da Silva, A.G.M.; Camargo, P.H.C. Nanocatalysis by noble metal nanoparticles: Controlled synthesis for the optimization and understanding of activities. *J. Mater. Chem. A* 2019, 7, 5857–5874. [CrossRef]
37. Pandey, S.; Do, J.Y.; Kim, J.; Kang, M. Fast and highly efficient catalytic degradation of dyes using κ-carrageenan stabilized silver nanoparticles nanocatalysts. *Carbohydr. Polym.* 2020, 230, 115597. [CrossRef] [PubMed]

38. Zhang, K.; Suh, J.M.; Choi, J.-W.; Jang, H.W.; Shokouhimehr, M.; Varma, R.S. Recent Advances in the Nanocatalyst-Assisted NaBH4 Reduction of Nitroaromatics in Water. *ACS Omega* 2019, 4, 483–495. [CrossRef]

39. Salam, N.; Banerjee, B.; Roy, A.S.; Mondal, P.; Roy, S.; Bhauvik, A.; Islam, S.K. Silver nanoparticles embedded over mesoporous organopolymer as highly efficient and reusable nanocatalyst for the reduction of nitroarenes and aerobic oxidative esterification of alcohols. *Appl. Catal. A Gen.* 2014, 477, 184–194. [CrossRef]

40. Hazlet, S.E.; Dornfeld, C.A. The Reduction of Aromatic Nitro Compounds with Activated Iron. *J. Am. Chem. Soc.* 1944, 66, 1781–1782. [CrossRef]

41. Zhu, K.; Shaver, M.P.; Thomas, S.P. Chemoselective nitro reduction and hydroamination using a single iron catalyst. *Chem. Sci.* 2016, 7, 3031–3035. [CrossRef]

42. Agrawal, A.; Tratnyek, P.G. Reduction of Nitro Aromatic Compounds by Zero-Valent Iron Metal. *Environ. Sci. Technol.* 1995, 30, 153–160. [CrossRef]

43. Chemistry—Stack Exchange. Preference for Tin or Iron in the Reduction of Nitrobenzene. Available online: https://chemistry.stackexchange.com/questions/110602/preference-for-tin-or-iron-in-the-reduction-of-nitrobenzene (accessed on 10 November 2020).

44. Popat, V.; Padihyar, N. Kinetic Study of Bechamp Process for P-Nitrotoluene Reduction to P-Toluidine. *Int. J. Chem. Eng. Appl.* 2013, 4, 401–405. [CrossRef]

45. Xu, L.; Wang, Y.-Y.; Huang, J.; Chen, C.-Y.; Wang, Z.-X.; Xie, H. Silver nanoparticles: Synthesis, medical applications and biosafety. *Theranostics* 2020, 10, 8996–9031. [CrossRef]

46. Castillo-Henriquez, L.; Alfaro-Aguilar, K.; Ugalde-Álvarez, J.; Vega-Fernández, L.; de Oca-Vásquez, G.M.; Vega-Baudrit, J.R. Green Synthesis of Gold and Silver Nanoparticles from Plant Extracts and Their Possible Applications as Antimicrobial Agents in the Agricultural Area. *Nanomaterials* 2020, 10, 1763. [CrossRef] [PubMed]

47. Hanan, N.A.; Chiu, H.I.; Ramachandran, M.R.; Tung, W.H.; Zain, N.N.M.; Yahaya, N.; Lim, V. Cytotoxicity of Plant-Mediated Synthesis of Metallic Nanoparticles: A Systematic Review. *Int. J. Mol. Sci.* 2018, 19, 1725. [CrossRef]

48. Fayez, H.; El-Motaleb, M.A.; Selim, A.A. Synergistic Cytotoxicity of Shikonin-Silver Nanoparticles as an Opportunity for Lung Cancer. *J. Label. Compd. Radiopharm.* 2020, 63, 25–32. [CrossRef] [PubMed]

49. Irvanani, S. Plant gums for sustainable and eco-friendly synthesis of nanoparticles: Recent advances. *Inorg. Nano-Met. Chem.* 2020, 50, 469–488. [CrossRef]

50. Siddiqui, M.Z.; Chowdhury, A.R.; Singh, B.R.; Maurya, S.; Prasad, N. Synthesis, Characterization and Antimicrobial Evaluation of Pijar Gum-Induced Silver Nanoparticles. *Natl. Acad. Sci. Lett.* 2020. [CrossRef]

51. Anwar, A.; Masri, A.; Rao, K.; Rajendran, K.; Khan, N.A.; Shah, M.R.; Siddiqui, R. Antimicrobial activities of green synthesized gums-stabilized nanoparticles loaded with flavonoids. *Sci. Rep.* 2019, 9, 3122. [CrossRef] [PubMed]

52. Thakur, M.; Pandey, S.; Mewada, A.; Shah, R.; Oza, G.; Sharan, M. Understanding the stability of silver nanoparticles bio-fabricated using *Acacia arabica* (Babool gum) and its hostile effect on microorganisms. *Spectrochim. Acta A* 2013, 109, 344–347. [CrossRef]

53. Gengan, R.M.; Phulukdaree, A.; Chuturgoon, A. A549 lung cell line activity of biosynthesized silver nanoparticles using *Albizia adianthifolia* leaf. *Colloids Surf. B* 2013, 105, 87–91. [CrossRef]

54. Niraimathi, K.L.; Sudha, V.; Lavanya, R.; Brindha, P. Biosynthesis of silver nanoparticles using *Alternanthera sessilis* (Linn.) extract and their antimicrobial, antioxidant activities. *Colloids Surf. B* 2013, 102, 288–291. [CrossRef]

55. Das, G.; Patra, J.K.; Deb Nath, T.; Ansari, A.; Shin, H.S. Investigation of antioxidant, antibacterial, antidiabetic, and cytotoxicity potential of silver nanoparticles synthesized using the outer peel extract of *Ananas comosus* (L.). *PLoS ONE* 2019, 14, e0220950. [CrossRef]

56. Vivek, R.; Thangam, R.; Muthuchelian, K.; Gunasekaran, P.; Kaveri, K.; Kannan, S. Green biosynthesis of silver nanoparticles from *Annona squamosa* leaf extract and its in vitro cytotoxic effect on MCF-7 cells. *Process Biochem.* 2012, 47, 2405–2410. [CrossRef]
57. Velusamy, P.; Das, J.; Pachaippan, R.; Vasheepran, B.; Pandian, K. Greener approach for synthesis of antibacterial silver nanoparticles using aqueous solution of neem gum (Azadirachta indica L.). Ind. Crop. Prod. 2015, 66, 103–109. [CrossRef]

58. Nazeruddin, G.M.; Prasad, N.R.; Waghmare, S.R.; Gadarkar, K.M.; Mulla, I.S. Extracellular biosynthesis of silver nanoparticle using Azadirachta indica leaf extract and its anti-microbial activity. J. Alloys Compd. 2014, 583, 272–277. [CrossRef]

59. Vijay Kumar, P.P.N.; Pammi, S.V.N.; Kollu, P.; Satyanarayana, K.V.V.; Shameem, U. Green synthesis and characterization of silver nanoparticles using Boerhaavia diffusa plant extract and their antibacterial activity. Ind. Crop. Prod. 2014, 52, 562–566. [CrossRef]

60. Ansar, S.; Tabassum, H.; Adawani, N.S.M.; Ali, M.N.; Almaroqui, B.; Almhrouri, S.; Abudawood, M.; Banu, N.; Alsubki, R. Eco friendly silver nanoparticles synthesis by Brassica oleracea and its antibacterial, anticaner and antioxidant properties. Sci. Rep. 2020, 10, 18564. [CrossRef]

61. Moteriya, P.; Chanda, S. Green Synthesis of Silver Nanoparticles from Caesalpinia pulcherrima Leaf Extract and Evaluation of Their Antimicrobial, Cytotoxic and Genotoxic Potential (3-in-1 System). J. Inorg. Organomet. Polym. 2020, 30, 3920–3932. [CrossRef]

62. Vinay, S.P.; Chandrasekhar, N. Green Synthesis and Characterization of Silver Nanoparticles using Cassia auriculata Leaves Extract and Its Efficacy as A Potential Antibacterial and Cytotoxic Effect. Adv. Mater. Lett. 2019, 10, 844–849. [CrossRef]

63. Balashanmugam, P.; Balakumaran, M.D.; Murugan, R.; Dhanapal, K.; Kalaichelvan, P.T. Phytoenic synthesis of silver nanoparticles, optimization and deevaluation of in vitro antifungal activity against human and plant pathogens. Microbiol. Res. 2016, 192, 52–64. [CrossRef]

64. Dhand, V.; Soumya, L.; Bharadwaj, S.; Chakra, S.; Bhatt, D.; Sreedhar, B. Green synthesis of silver nanoparticles using Coffea arabica seed extract and its antibacterial activity. Mater. Sci. Eng. C 2016, 58, 36–43. [CrossRef]

65. Alwhibi, M.S.; Soliman, D.A.; Khaldy, H.; Alonazain, A.; Marraiki, N.A.; El-Zaied, M.; AlSubeie, M.S. Green biosynthesis of silver nanoparticles using Comminophora myrrha extract and evaluation of their antimicrobial activity and colon cancer cells viability. J. King Saud Univ. Sci. 2020, 32, 3372–3379. [CrossRef]

66. Ahmad, A.; Wei, Y.; Syed, F.; Tahir, K.; Rehman, A.U.; Khan, A.; Ullah, S.; Yuan, Q. The effects of bacteria-nanoparticles interface on the antibacterial activity of green synthesized silver nanoparticles. Microb. Pathog. 2017, 102, 133–142. [CrossRef] [PubMed]

67. Hemlata; Meena, P.R.; Singh, A.P.; Tejavath, K.K. Biosynthesis of Silver Nanoparticles Using Cucumis prophetarum Aqueous Leaf Extract and Their Antibacterial and Anti proliferative Activity Against Cancer Cell Lines. ACS Omega 2020, 5, 5520–5528. [CrossRef] [PubMed]

68. Gajendran, B.; Chinnasamy, A.; Durai, P.; Raman, J.; Ramar, M. Biosynthesis and characterization of silver nanoparticles from Datura inoxia and its apoptotic effect on human breast cancer cell line MCF7. Mater. Lett. 2014, 122, 98–102. [CrossRef] [PubMed]

69. Suresh, G.; Gunasekar, P.H.; Kokila, D.; Prabhu, D.; Dinesh, D.; Ravichandran, N.; Ramesh, B.; Koodalingam, A.; Siva, G.V. Green synthesis of silver nanoparticles using Delphinium denudatum root extract exhibits antibacterial and mosquito larvicidal activities. Spectrochim. Acta A 2014, 127, 61–66. [CrossRef] [PubMed]

70. Hamed, S.; Shojasadati, S.A. Rapid and green synthesis of silver nanoparticles using Diospyros lotus extract: Evaluation of their biological and catalytic activities. Polyhedron 2019, 171, 172–180. [CrossRef] [PubMed]

71. Ramesh, P.S.; Kokila, T.; Geetha, D. Plant mediated green synthesis and antibacterial activity of silver nanoparticles using Emblica officinalis fruit extract. Spectrochim. Acta A 2015, 142, 339–343. [CrossRef] [PubMed]

72. Rathi Sre, P.R.; Reka, M.; Poovazhagi, R.; Arul Kumar, M.; Murugesan, K. Antibacterial and cytotoxic effect of biologically synthesized silver nanoparticles using aqueous root extract of Erythrina indica lam. Spectrochim. Acta A 2015, 135, 1137–1144. [CrossRef]

73. Huang, L.; Sun, Y.; Mahmud, S.; Liu, H. Biological and Environmental Applications of Silver Nanoparticles Synthesized Using the Aqueous Extract of Ginkgo biloba Leaf. J. Inorg. Organomet. Polym. Mater. 2020, 30, 1653–1668. [CrossRef]

74. Xu, Z.; Feng, Q.; Wang, M.; Zhao, H.; Lin, Y.; Zhou, S. Green Biosynthesized Silver Nanoparticles With Aqueous Extracts of Ginkgo Biloba Induce Apoptosis via Mitochondrial Pathway in Cervical Cancer Cells. Front. Oncol. 2020, 10, 575415. [CrossRef]
75. Sana, S.S.; Badineni, V.R.; Arla, S.K.; Boya, V.K.N. Eco-friendly synthesis of silver nanoparticles using leaf extract of *Grevia flavescentis* and study of their antimicrobial activity. *Mater. Lett.* **2015**, *145*, 347–350. [CrossRef]

76. Netala, V.R.; Bukke, S.; Domdi, L.; Soneya, S.; Reddy, S.G.; Bethu, M.S.; Kotakdi, V.S.; Saritha, K.V.; Tartte, V. Biogenesis of silver nanoparticles using leaf extract of *Indigofera hirsuta* L. and their potential biomedical applications (3-in-1 system). *Artif. Cells Nanomed. Biotechnol.* **2018**, *46*, 1138–1148. [CrossRef] [PubMed]

77. Basumatary, K.; Daimary, P.; Das, S.K.; Thapa, M.; Singh, M.; Mukherjee, A.; Kumar, S. Lagerstroemia speciosa fruit-mediated synthesis of silver nanoparticles and its application as filler in agar based nanocomposite films for antimicrobial food packaging. *Food Packag. Shelf Life* **2018**, *17*, 99–106. [CrossRef]

78. Sekhar, E.C.; Rao, K.S.V.K.; Rao, K.M.; Kumar, S.P. A green approach to synthesize controllable silver nanostructures from *Limonia acidissima* for inactivation of pathogenic bacteria. *Cogent Chem.* **2016**, *2*, 1144296. [CrossRef]

79. Lokina, S.; Stephen, A.; Kaviyarasan, V.; Arulvasu, C.; Narayanan, V. Cytotoxicity and antimicrobial activities of green synthesized silver Nanoparticles. *Eur. J. Med. Chem.* **2014**, *76*, 256–263. [CrossRef] [PubMed]

80. Kamaraj, C.; Rajakumar, G.; Rahuman, A.A.; Velayutham, K.; Bagavan, A.; Zahir, A.A.; Elango, G. Feeding deterrent activity of synthesized silver nanoparticles using *Manilkara zapota* leaf extract against the house fly, *Musca domestica* (Diptera: Muscidae). *Parasitol. Res.* **2012**, *111*, 2439–2448. [CrossRef]

81. Sukirtha, R.; Priyanka, K.M.; Antony, J.J.; Kamalakkannan, S.; Thangam, R.; Gunasekaran, P.; Krishnan, M.; Achiraman, S. Cytotoxic effect of Green synthesized silver nanoparticles using *Melia azedarach* against in vitro HeLa cell lines and lymphoma mice model. *Process Biochem.* **2012**, *47*, 273–279. [CrossRef]

82. Suman, T.Y.; Rajasree, S.R.R.; Kanchana, A.; Elizabeth, S.B. Biosynthesis, characterization and cytotoxic effect of plant mediated silver nanoparticles using *Morinda citrifolia* root extract. *Colloids Surf. B* **2013**, *106*, 74–78. [CrossRef]

83. Sankar, R.; Karthik, A.; Prabu, A.; Karthik, S.; Shivashangari, K.S.; Ravikumar, V. *Oignonum vulgare* mediated biosynthesis of silver nanoparticles for its antibacterial and anticancer activity. *Colloids Surf. B BioInterfaces* **2013**, *108*, 80–84. [CrossRef]

84. Mohammed, A.E.; Al-Qahtani, A.; Al-Mutairi, A.; Al-Shamri, B.; Aabed, K. Antibacterial and Cytotoxic Potential of Biosynthesized Silver Nanoparticles by Some Plant Extracts. *Nanomaterials* **2018**, *8*, 382. [CrossRef]

85. Jacob, S.J.P.; Finub, J.S.; Narayanan, A. Synthesis of silver nanoparticles using *Piper longum* leaf extracts and its cytotoxic activity against Hep-2 cell line. *Colloids Surf. B* **2012**, *91*, 212–214. [CrossRef]

86. Ajitha, B.; Reddy, Y.A.K.; Reddy, P.S. Biosynthesis of silver nanoparticles using *Plectranthus amboinicus* leaf extract and its antimicrobial activity. *Spectrochim. Acta A* **2014**, *128*, 257–262. [CrossRef] [PubMed]

87. Mittal, A.K.; Tripathy, D.; Choudhary, A.; Aili, P.K.; Chatterjee, A.; Singh, I.P.; Banerjee, U.C. Bio-synthesis of silver nanoparticles using *Potentilla fulgens* Wall. ex.Hook. and its therapeutic evaluation as anticancer and antimicrobial agent. *Mater. Sci. Eng. C* **2015**, *53*, 120–127. [CrossRef] [PubMed]

88. Raja, K.; Saravananukumar, A.; Vijayakumar, R. Efficient synthesis of silver nanoparticles from *Prosopis juliflora* leaf extract and its antimicrobial activity using sewage. *Spectrochim. Acta A* **2012**, *97*, 490–494. [CrossRef] [PubMed]

89. Devanesan, S.; AlSalhi, M.S.; Balaji, R.V.; Ranjitsingh, A.J.A.; Ahamed, A.; Alfuraydi, A.A.; AlQahtani, F.Y.; Aleanizy, F.S.; Othman, A.H. Antimicrobial and Cytotoxicity Effects of Synthesized Silver Nanoparticles from *Punica granatum* Peel Extract. *Nanoscale Res. Lett.* **2018**, *13*, 315. [CrossRef] [PubMed]

90. Reddy, P.R.; Ganesh, S.D.; Saha, N.; Zandraa, O.; Saha, P. Ecofriendly Synthesis of Silver Nanoparticles from *Garden Rhubarb* (*Rheum rhabarbarum*). *J. Nanotechnol.* **2016**, *2016*, 4964752. [CrossRef]

91. Palem, R.R.; Ganesh, S.D.; Kronekova, Z.; Slavikova, M.; Saha, N.; Saha, P. Green synthesis of silver nanoparticles and biopolymer nanocomposites: A comparative study on physico-chemical, antimicrobial and anticancer activity. *Bull. Mater. Sci.* **2018**, *41*, 55. [CrossRef]

92. Palem, R.R.; Saha, N.; Shimoga, G.D.; Kronekova, Z.; Slavikova, M.; Saha, P. Chitosan–silver nanocomposites: New functional biomaterial for health-care applications. *Int. J. Polym. Mater.* **2018**, *67*, 1–10. [CrossRef]

93. Dobrucka, R.; Kaczmarek, M.; Dlugaszewska, J. Cytotoxic and antimicrobial effect of biosynthesized silver nanoparticles using the fruit extract of *Ribes nigrum*. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2018**, *9*, 025015. [CrossRef]
94. Daghestani, M.; Al Rashed, S.A.; Bukhari, W.; Al-Ojayan, B.; Ibrahim, E.M.; Al-Qahtani, A.M.; Merghani, N.M.; Ramadan, R.; Bhat, R.S. Bactericidal and cytotoxic properties of green synthesized nanosilver using *Rosmarinus officinalis* leaves. *Green Process. Synth.* 2020, 9, 230–236. [CrossRef]

95. Dayanidhi, K.; Vadivel, P.; Jothi, S.; Eusuff, N.S. Facile synthesis of Silver@Eggshell nanocomposite: A heterogeneous catalyst for the removal of heavy metal ions, toxic dyes and microbial contaminants from water. *J. Environ. Manag.* 2020, 271, 110962. [CrossRef]

96. Palanisamy, S.; Rajasekar, P.; Vijayarajprasath, G.; Ravi, G.; Manikandan, R.; Prabhu, N.M. A green route to synthesis silver nanoparticles using *Sargassum polycystum* and its antioxidant and cytotoxic effects: An in vitro analysis. *Mater. Lett.* 2017, 189, 196–200. [CrossRef]

97. Ramar, M.; Manikandan, B.; Marimuthu, P.N.; Raman, T.; Mahalingam, A.; Subramanian, P.; Karthick, S.; Munusamy, A. Synthesis of silver nanoparticles using *Solanum trilobatum* fruits extract and its antibacterial, cytotoxic activity against human breast cancer cell line MCF 7. *Spectrochim. Acta A* 2015, 140, 223–228. [CrossRef]

98. Venugopal, K.; Rather, H.A.; Rajagopal, K.; Shanthi, M.P.; Sherlock, K.; Illyas, M.; Rather, R.A.; Manikandan, E.; Uvarajan, S.; Bhaskar, M.; et al. Synthesis of silver nanoparticles (Ag NPs) for anticancer activities (MCF 7 breast and A549 lung cell lines) of the crude extract of *Syzygium aromaticum*. *J. Photochem. Photobiol. B Biol.* 2017, 167, 282–289. [CrossRef] [PubMed]

99. Espenti, C.S.; Rao, K.S.V.K.; Rao, K.M. Bio-synthesis and characterization of silver nanoparticles using *Terminalia chebula* leaf extract and evaluation of its antimicrobial potential. *Mater. Lett.* 2016, 174, 129–133. [CrossRef]

100. Sharma, V.; Kaushik, S.; Pandit, P.; Dhull, D.; Yadav, J.P.; Kaushik, S. Green synthesis of silver nanoparticles from medicinal plants and evaluation of their antiviral potential against chikungunya virus. *Appl. Microbiol. Biotechnol.* 2019, 103, 881–891. [CrossRef]

101. Iravani, S.; Korbekandi, H.; Mimohammadi, S.V.; Zolfaghari, B. Synthesis of silver nanoparticles: Chemical, physical and biological methods. *Res. Pharm. Sci.* 2014, 9, 385–406.

102. Hamouda, R.A.; Hussein, M.H.; Abo-elmagd, R.A.; Bawazir, S.S. Synthesis and biological characterization of silver nanoparticles from medicinal plants and evaluation of their antimicrobial activity. *Sci. Rep.* 2019, 9, 13071. [CrossRef]

103. Franci, G.; Falanga, A.; Galdiero, S.; Palomba, L.; Rai, M.; Morelli, G. Silver Nanoparticles as Potential Antibacterial Agents. *Molecules* 2015, 20, 8858–8874. [CrossRef]

104. Sarsar, V.; Selwal, K.K.; Selwal, M.K. Nanosilver: Potent antimicrobial agent and its biosynthesis. *Afr. J. Biotechnol.* 2014, 13, 546–554. [CrossRef]

105. Rajeshkumar, S.; Bharath, L.V. Mechanism of plant-mediated synthesis of silver nanoparticles—A review on biomolecules involved, characterisation and antibacterial activity. *Chem. Biol. Interact.* 2017, 273, 219–227. [CrossRef]

106. Lade, B.D.; Shanware, A.S. *Phytonanofabrication: Methodology and Factors Affecting Biosynthesis of Nanoparticles*; IntechOpen, 2020. Available online: https://www.intechopen.com/books/smart-nanosystems-for-biomedicine-optoelectronics-and-catalysis/phytonanofabrication-methodology-and-factors-affecting-biosynthesis-of-nanoparticles (accessed on 9 December 2020). [CrossRef]

107. National Ocean Service. Contaminants in the Environment. Available online: https://oceanservice.noaa.gov/observations/contam/#:~:text=Most%20contaminants%20enter%20the%20environment%20from%20plants%20and%20sewage%20systems (accessed on 11 November 2020).

108. Thompson, L.A.; Darwish, W.S. Environmental Chemical Contaminants in Food: Review of a Global Problem. *J. Toxicol.* 2019, 2019, 2345283. [CrossRef] [PubMed]

109. Bhunia, P. Environmental Toxicants and Hazardous Contaminants: Recent Advances in Technologies for Sustainable Development. *J. Hazard. Toxic Radioact. Waste* 2017, 21, 02017001. [CrossRef]

110. Rout, P.R.; Bhunia, P. Assessing Possible Applications of Waste Organic Solid Substances as Carbon Sources and Biofilm Substrates for Elimination of Nitrate Toxicity from Wastewater. *J. Hazard. Toxic Radioact. Waste* 2017, 21, 04016027. [CrossRef]

111. The World Bank. What You Need to Know about Toxic Pollution: A Conversation with Richard Fuller. Available online: https://www.worldbank.org/en/news/feature/2015/04/21/what-you-need-to-know-about-toxic-pollution-a-conversation-with-richard-fuller (accessed on 11 November 2020).
112. Uberoi, V.; Bhattacharya, S.K. Toxicity and Degradability of Nitrophenols in Anaerobic Systems. *Water Environ. Res.* 1997, 69, 146–156. [CrossRef]

113. Agency for Toxic Substances and Disease Registry. Toxicological Profile for Nitrophenols: 2-Nitrophenol, 4-Nitrophenol. Available online: https://www.atsdr.cdc.gov/toxprofiles/tp50.pdf (accessed on 11 November 2020).

114. Subhashchandrabose, S.R.; Megharaj, M.; Venkateshwari, K.; Naidu, R. p-Nitrophenol toxicity to and its removal by three select soil isolates of microalgae: The role of antioxidants. *Environ. Chem.* 2012, 31, 1980–1988. [CrossRef]

115. Biodegradation. Research Watch: Nitrophenol toxicity. *Environ. Sci. Technol.* 1997, 31, 259A. [CrossRef]

116. Agency for Toxic Substances and Disease Registry. Toxicological Profile for Nitrobenzene. Available online: https://www.atsdr.cdc.gov/toxprofiles/tp140.pdf (accessed on 11 November 2020).

117. Material Safety Data Sheet. 4-Nitrophenol. Available online: https://datasheets.scbt.com/sc-206922.pdf (accessed on 11 November 2020).

118. Duda, J.M.W. Phenols—Sources and Toxicity. *Pol. J. Environ. Stud.* 2007, 16, 347–362. Available online: http://www.pipes.com/pdf/87995-21854?filename=Phenols%20%20Sources%20and.pdf (accessed on 11 November 2020).

119. Šljukić, B.; Santos, D.M.; Sequeira, C.A.C.; Banks, C.E. Analytical monitoring of sodium borohydride. *Anal. Methods* 2013, 5, 829–839. [CrossRef]

120. Davis, R.E.; Swain, C.G. General acid catalysis of the hydrolysis of sodium borohydride. *J. Am. Chem. Soc.* 1960, 82, 5949–5950. [CrossRef]

121. Schlesinger, H.I.; Brown, H.C.; Finholt, A.E.; Gilbreath, J.R.; Hoekstra, H.R.; Hyde, E.K. Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen. *J. Am. Chem. Soc.* 1953, 75, 215–219. [CrossRef]

122. Kong, X.; Zhu, H.; Chen, C.; Huang, G.; Chen, Q. Insights into the reduction of 4-nitrophenol to 4-aminophenol on catalysts. *Chem. Phys. Lett.* 2017, 684, 148–152. [CrossRef]

123. Kästner, C.; Thünemann, A.F. Catalytic Reduction of 4-Nitrophenol Using Silver Nanoparticles with Adjustable Activity. *Langmuir* 2016, 32, 7383–7391. [CrossRef] [PubMed]

124. Thawarkar, S.R.; Thombare, B.; Munde, B.S.; Khupse, N.D. Kinetic investigation for the catalytic reduction of nitrophenol using ionic liquid stabilized gold nanoparticles. *RSC Adv.* 2018, 8, 38384–38390. [CrossRef]

125. Ayad, A.I.; Luart, D.; Dris, A.O.; Guénin, E. Kinetic Analysis of 4-Nitrophenol Reduction by “Water-Soluble” Palladium Nanoparticles. *Nanomaterials* 2020, 10, 1169. [CrossRef] [PubMed]

126. Bhaduri, B.; Polubesova, T. Facile synthesis of carbon-supported silver nanoparticles as an efficient reduction catalyst for aqueous 2-methyl-п-nitrophenol. *Material Letters* 2020, 267, 127546. [CrossRef]

127. Priya, D.B.; Asharani, I.V. Size Dependent Catalytic Activity of Actinodaphne madraspatana Bedd Leaves Mediated Silver Nanoparticles. *J. Clust. Sci.* 2017, 28, 1837–1856. [CrossRef]

128. Ismail, M.; Khan, M.I.; Khan, S.B.; Akhtar, K.; Khan, M.A.; Asiri, A.M. Catalytic reduction of picric acid, nitrophenols and organic azo dyes via green synthesized plant supported Ag nanoparticles. *J. Mol. Liq.* 2018, 268, 87–101. [CrossRef]

129. Ko, J.W.; Ko, W.B. Catalytic Activity for Reduction of 4-Nitrophenol with [C60] Fullerene Nanowhisker-Silver Nanoparticle Composites. *Mater. Trans.* 2016, 57, 2122–2126. [CrossRef]

130. Corbet, J.F. Pseudo first-order kinetics. *J. Chem. Educ.* 1972, 49, 663. [CrossRef]

131. Kalantari, K.; Affi, A.B.M.; Bayat, S.; Shamlou, K.; Yousefi, S.; Mokhtar, N.; Kalantari, A. Heterogeneous catalysis in 4-nitrophenol degradation and antioxidant activities of silver nanoparticles embedded in Tapioca starch. *Arab. J. Chem.* 2019, 8, 5243–5252. [CrossRef]

132. Irvine, W.M. Langmuir-Hinshelwood Mechanism. In Encyclopedia of Astrobiology; Gargaud, M., Amils, R., Quintanilla, C., Cleaves, H.J., Irvine, W.M., Pinti, D., Viso, M., Eds.; Springer: Berlin/Heidelberg, Germany, 2011. [CrossRef]

133. Gavade, S.J.M.; Nikam, G.H.; Sabale, S.R.; Tamhankar, B.V. Green synthesis of fluorescent silver nanoparticles using *Acacia nilotica* gum extract for kinetic studies of 4-nitrophenol reduction. *Mater. Today Proc.* 2016, 3, 4109–4114. [CrossRef]
135. Shah, Z.; Hassan, S.; Shaheen, K.; Khan, S.A.; Gul, T.; Anwar, Y.; Al-shaeri, M.A.; Khan, M.; Khan, R.; Haleem, M.A.; et al. Synthesis of AgNPs coated with secondary metabolites of Acacia nilotica: An efficient antimicrobial and detoxification agent for environmental toxic organic pollutants. *Mater. Sci. Eng. C* 2020, 111, 110829. [CrossRef] [PubMed]

136. Manjari, G.; Saran, S.; Arun, T.; Deviipriya, S.P.; Rao, A.V.B. Facile Aglaia elaeagnoides Mediated Synthesis of Silver and Gold Nanoparticles: Antioxidant and Catalysis Properties. *J. Clust. Sci.* 2017, 28, 2041–2056. [CrossRef]

137. Gangarapu, M.; Sarangapany, S.; Veerabhali, K.K.; Deviipriya, S.P.; Arava, V.B.R. A High-Performance Catalytic and Recyclability of Phytosynthesized Silver Nanoparticles Embedded in Natural Polymer. *J. Clust. Sci.* 2017, 28, 3127–3138. [CrossRef]

138. Khoshnamvand, M.; Huo, C.; Liu, J. Silver nanoparticles synthesized using Allium ampeloprasum L. leaf extract: Characterization and performance in catalytic reduction of 4-nitrophenol and antioxidant activity. *J. Mol. Struct.* 2019, 1175, 90–96. [CrossRef]

139. Nguyen, T.T.N.; Vo, T.T.; Nguyen, B.N.H.; Nguyen, D.T.; Dang, V.S.; Dang, C.H.; Nguyen, T.D. Silver and gold nanoparticles biosynthesized by aqueous extract of burdock root, *Arctium lappa* as antimicrobial agent and catalyst for degradation of pollutants. *Environ. Sci. Pollut. Res.* 2018, 25, 34247–34261. [CrossRef] [PubMed]

140. Nasrollahzadeh, M.; Issaabadi, Z.; Sajadi, S.M. Green synthesis of the Ag/Al2O3 nanoparticles using Bryonia alba leaf extract and their catalytic application for the degradation of organic pollutants. *J. Mater. Sci. Mater. Electron.* 2019, 30, 3847–3859. [CrossRef]

141. Abouelfetoh, E.F.; El-Shenody, R.A.; Ghobara, M.M. Eco-friendly synthesis of silver nanoparticles using green algae (Caulerpa serrulata): Reaction optimization, catalytic and antibacterial activities. *Environ. Monit. Assess.* 2017, 189, 349. [CrossRef]

142. Eze, F.N.; Tola, A.J.; Nwabor, O.F.; Jayeoye, T.J. Centella asiatica phenolic extract-mediated biofabrication of silver nanoparticles: Characterization, reduction of industrially relevant dyes in water and antimicrobial activities against foodborne pathogens. *RSC Adv.* 2019, 9, 37957. [CrossRef]

143. Arya, G.; Sharma, N.; Ahmed, J.; Gupta, N.; Kumar, A.; Chandra, R.; Nimesh, S. Degradation of anthropogenic pollutant and organic dyes by biosynthesized silver nano-catalyst from Cicer arietinum leaves. *J. Photochem. Photobiol. B Biol.* 2017, 174, 90–96. [CrossRef]

144. Bordbar, M.; Mortazavimanesk, N. Biosynthesis of waste pistachio shell supported silver nanoparticles for the catalytic reduction processes. *IET Nanobiotechnol.* 2018, 12, 939–945. [CrossRef] [PubMed]

145. Naraginti, S.; Sivakumar, A. Eco-friendly synthesis of silver and gold nanoparticles with enhanced bactericidal activity and study of silver catalyzed reduction of 4-nitrophenol. *Spectrochim. Acta A* 2014, 128, 357–362. [CrossRef] [PubMed]

146. Denrah, S.; Sarkar, M. Design of experiment for optimization of nitrophenol reduction by green synthesized silver nanocatalyst. *Chem. Eng. Res. Des.* 2019, 114, 494–504. [CrossRef]

147. Muniyappan, N.; Nagarajan, N.S. Green synthesis of silver nanoparticles with *Dalbergia spinosa* leaves and their applications in biological and catalytic activities. *Process Biochem.* 2014, 49, 1054–1061. [CrossRef]

148. Ismail, M.; Khan, M.I.; Khan, M.A.; Akhtar, K.; Asiri, A.M.; Khan, S.B. Plant-supported silver nanoparticles: Efficient, economically viable and easily recoverable catalyst for the reduction of organic pollutants. *Appl. Organomet. Chem.* 2019, 33, e4971. [CrossRef]

149. Wang, F.; Zhang, W.; Tan, X.; Wang, Z.; Li, Y.; Li, W. Extract of Ginkgo biloba leaves mediated biosynthesis of catalytically active and recyclable silver nanoparticles. *Colloids Surf. A* 2019, 563, 31–36. [CrossRef]

150. Vartooni, A.R.; Nasrollahzadeh, M.; Alizadeh, M. Green synthesis of perlite supported silver nanoparticles using Hamamelis virginiana leaf extract and investigation of its catalytic activity for the reduction of 4-nitrophenol and Congo red. *J. Alloy. Compd.* 2016, 680, 309–314. [CrossRef]

151. Ajitha, B.; Reddy, Y.A.K.; Reddy, P.S.; Suneetha, Y.; Jeon, H.-J.; Ahn, C.W. Instant biosynthesis of silver nanoparticles using Lawsonia inermis leaf extract: Innate catalytic, antimicrobial and antioxidant activities. *J. Mol. Liq.* 2016, 219, 474–481. [CrossRef]

152. Rani, P.; Kumar, V.; Singh, P.P.; Matharu, A.S.; Zhang, W.; Kim, K.-H.; Singh, J.; Rawat, M. Highly stable AgNPs prepared via a novel green approach for catalytic and photocatalytic removal of biological pollutants. *Environ. Int.* 2020, 143, 105924. [CrossRef]
153. Edison, T.J.I.; Sethuraman, M.G. Biogenic robust synthesis of silver nanoparticles using Punica granatum peel and its application as a green catalyst for the reduction of an anthropogenic pollutant 4-nitrophenol. Spectrochim. Acta A 2013, 104, 262–264. [CrossRef]

154. Muthu, K.; Rajeswari, S.; Akilandaesanwari, B.; Nagasundari, S.M.; Rangasamy, R. Synthesis, characterisation and photocatalytic activity of silver nanoparticles stabilised by Punica granatum seeds extract. Mater. Technol. 2020. [CrossRef]

155. Palem, R.R.; Shimoga, G.; Kang, T.J.; Lee, S.-H. Fabrication of multifunctional Guar gum-silver nanocomposite hydrogels for biomedical and environmental applications. Int. J. Biol. Macromol. 2020, 159, 474–486. [CrossRef] [PubMed]

156. Rokade, A.A.; Kim, J.H.; Lim, S.R.; Yoo, S.I.; Jin, Y.E.; Park, S.S. A Novel Green Synthesis of Silver Nanoparticles Using Rubus crataegifolius Bge Fruit Extract. J. Clust. Sci. 2017, 28, 2017–2026. [CrossRef]

157. Vellaichamy, B.; Periakaruppan, P. Silver-nanospheres as a green catalyst for the decontamination of hazardous pollutants. RSC Adv. 2015, 5, 105917–105924. [CrossRef]

158. Veisi, H.; Kazemi, S.; Mohammad, M.; Safarimehr, P.; Hemmati, S. Catalytic reduction of 4-nitrophenol over Ag nanoparticles immobilized on Stachys Lavandulifolia extract-modified multi walled carbon nanotubes. Polyhedron 2019, 157, 232–240. [CrossRef]

159. Ajitha, B.; Reddy, Y.A.K.; Lee, Y.; Kim, M.J.; Ahn, C.W. Biomimetic synthesis of silver nanoparticles using Syzygium aromaticum (clove) extract: Catalytic and antimicrobial effects. Appl. Organomet. Chem. 2019, 33, e4867. [CrossRef]

160. Sherin, L.; Sohail, A.; Amjad, U.S.; Mustafa, M.; Jabeen, R.; Ul-Hamid, A. Facile green synthesis of silver nanoparticles using Terminalia bellerica kernel extract for catalytic reduction of anthropogenic water pollutants. Colloids Interface Sci. Commun. 2020, 37, 100276. [CrossRef]

161. Veisi, H.; Azizi, S.; Mohammadi, P. Green synthesis of the silver nanoparticles mediated by Thymbra spicata extract and its application as a heterogeneous and recyclable nanocatalyst for catalytic reduction of a variety of dyes in water. J. Clean. Prod. 2018, 170, 1536–1543. [CrossRef]

162. Singh, J.; Mehta, A.; Rawat, M.; Basu, S. Green synthesis of silver nanoparticles using sun dried tulsi leaves and its catalytic application for 4-Nitrophenol reduction. J. Environ. Chem. Eng. 2018, 6, 1468–1474. [CrossRef]

163. Zayed, M.F.; Eisa, W.H.; Abdel-Moneam, Y.K.; El-kousy, S.M.; Atia, A. Ziziphus spina-christi based bio-synthesis of Ag nanoparticles. J. Ind. Eng. Chem. 2015, 23, 50–56. [CrossRef]

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.