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Catalytic Degradability of *p*-Nitrophenol Using Ecofriendly Silver Nanoparticles

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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 beneficiality 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 subtilus* 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	NR	A549 cells	[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	NR	[64]
Commiphora myrrha	Plant	0.5–25.0	445.0	Effective	SW480 cells	[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	NR	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 & HEPG$_2$ 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)	Ultraviolet-Visible Spectroscopy (UV-Vis) RANGE	Antimicrobial Activity	Cytotoxicity Effective on	References
		(nm)	(nm)			
Origanum vulgare	Leaves	136.0	440.0	NR	A549 cell	[83]
Phoenix dactylifera, Ferula asafetida, 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]
Rheum rhabarbarum + Chitosan	Stems	5.0–50.0	430.0–450.0	Effective	HeLa	[92]
Ribes nigrum	Fruits	5.0–10.0	450.0	Effective	A549 cells	[93]
Rosmarinus officinalis	Leaves	12.0–22.0	400.0	Effective	MDA MB 231	[94]
Sapindus mukorossi	Extract	35.0	420.0	Effective	NR	[95]
Sargassum polycystum		28.0	405.0	NR	HT-29 cells	[96]
Solanum trilobatum	Fruits	12.0–41.0	432.0	Effective	MCF 7	[97]
Syzygium aromaticum	Cloves	5.0–40.0	441.0	NR	MCF 7 & A549	[98]
Terminaliachebula	Leaves	10.0–30.0	421.0	Effective	NR	[99]

NR = Not reported.

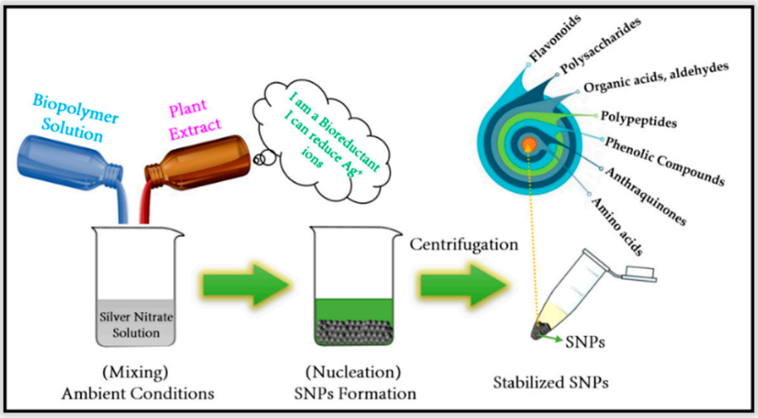

Figure 1. Phyto-synthesis and stability of silver nanoparticles (SNPs) in combination with biopolymers.

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).

3. Catalytic Degradation of *p*-Nitrophenol Using Silver Nanoparticles

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 H_3BO_3/BH_4^- 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).

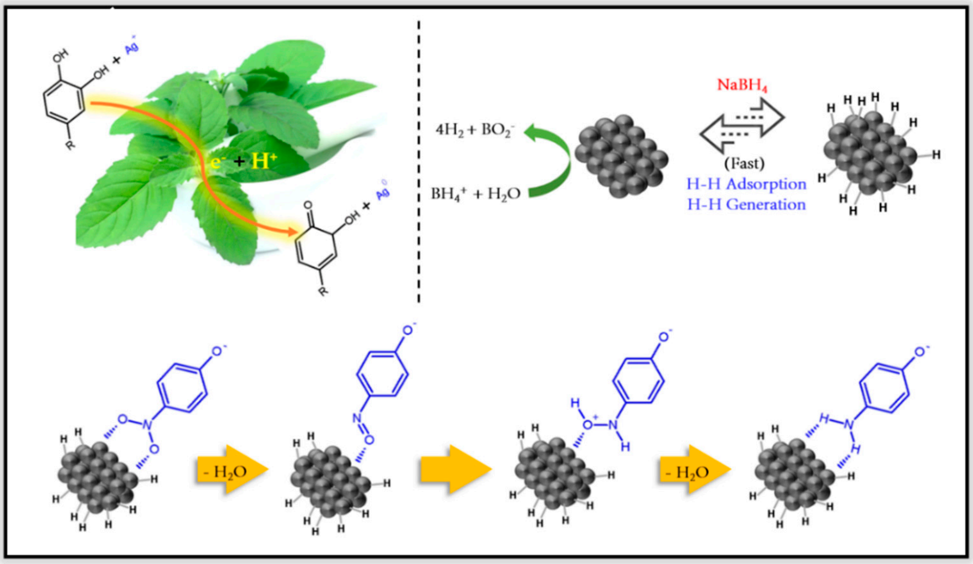

Figure 2. Phyto-synthesis of SNPs and catalytic reduction of *p*-nitrophenol (PNP) on SNPs surface in presence of sodium borohydride.

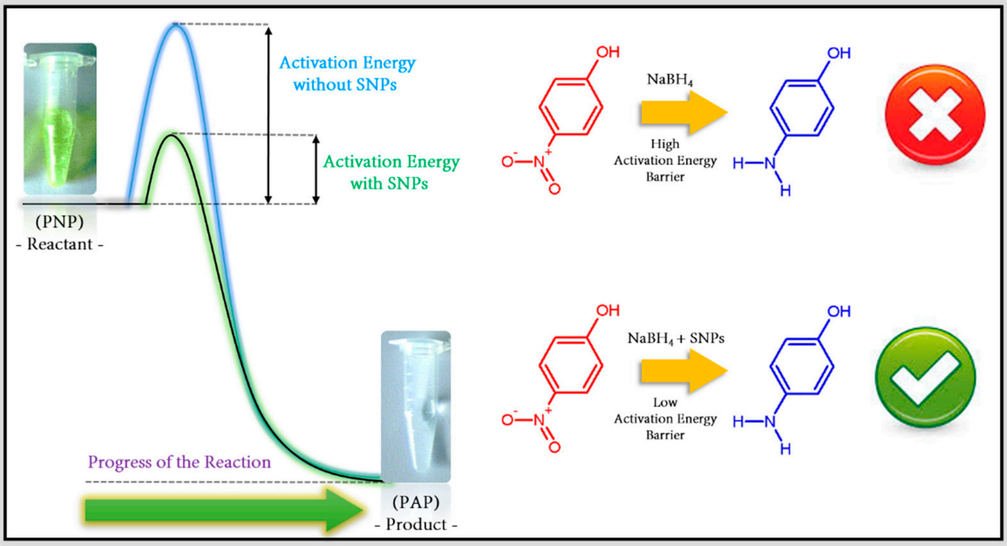

Figure 3. Graphical representation of activation energy and catalytic reduction of PNP to *p*-aminophenol (PAP).

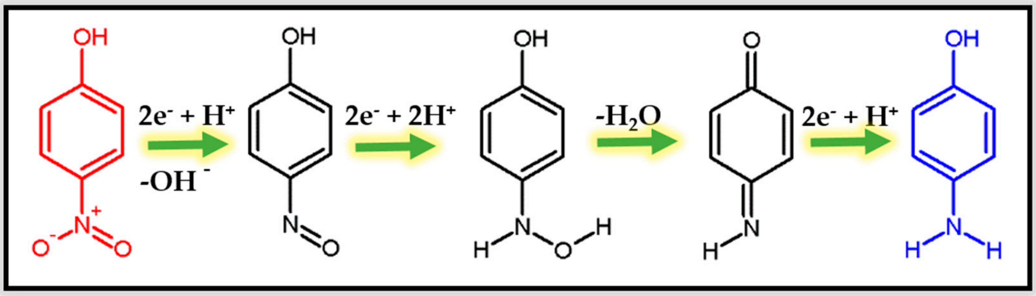

Figure 4. Involvement of six-electron in the conversion reaction of PNP to PAP. Adapted from [128], with permission from Elsevier, 2018.

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 ($\lambda_{\max}$) 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 $\lambda_{\max}$ = 400–410 nm was observed with the appearance of new $\lambda_{\max}$ 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:

$$-k_1\mathrm{S} = -k_{app}\,t = \ln\frac{C_t}{C_0}$$

where k_{app} (k_1S = 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_{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 °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)	BH_4^- (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	0.1	5.0	13.25×10^{-3} s^{-1}	[127]
Aglaia elaeagnoidea (Flowers)	17.0	NR	15.0	1.0	10.0	22.5×10^{-2} min^{-1}	[136]
Aglaia 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^{-3} 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	NR	21.5	21.5	3.9×10^{-3} s^{-1}	[142]
Cicer arietinum (Leaves)	88.8	30.0 µg	40.0	2.0	30.0	NR	[143]
Cichorium 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	10	50.0	0.10118 min^{-1}	[145]
Colocasia esculenta (Rhizome)	68.0	3.3 mg	6.0	1.0	500	5.27×10^{-3} s^{-1}	[128]
Cyperus Rotundus (Rhizome)	10.0–40.0	100.0 µL	10.0	5.0	100.0	0.293 min^{-1}	[146]
Dalbergia spinosa (Leaves)	18.0	200.0 µL	40.0	0.1	0.1	NR	[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]
Lawsonia Inermis (Leaves)	18.0	20.0 µL	15.0	1.0	1.0	NR	[151]
Phaseolus vulgaris (Beans)	10.0–20.0	1590.0 nM	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 (Cloves)	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 as nanocatalysts against model reduction reaction of PNP to PAP by aqueous sodium borohydride with apparent rate constant of 121.8×10^{-3} 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.

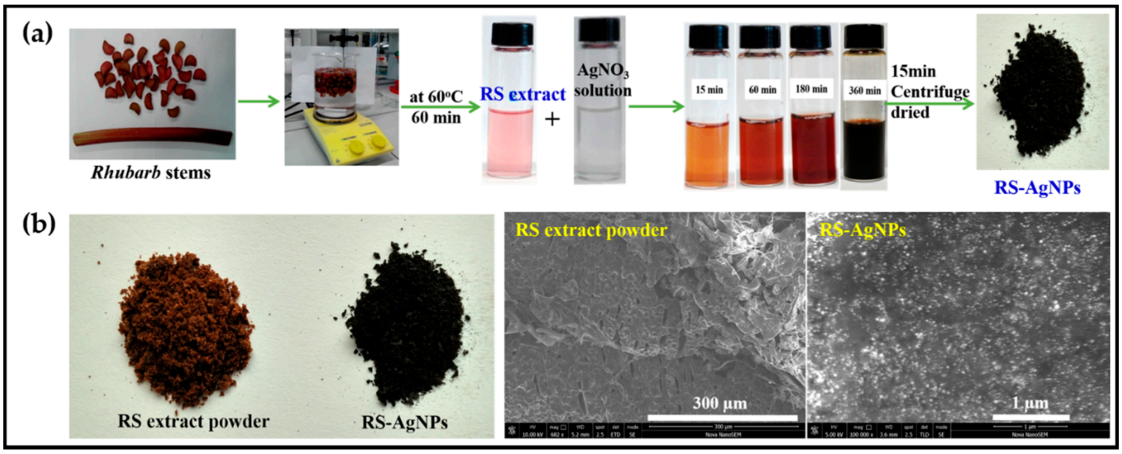

Figure 5. (**a**) Synthesis of RS-AgNPs from *Rhubarb* stem extract (RS extract), (**b**) Pictograph and SEM morphology of RS extract and RS-AgNPs. Adopted from [91], with permission from Springer, 2018.

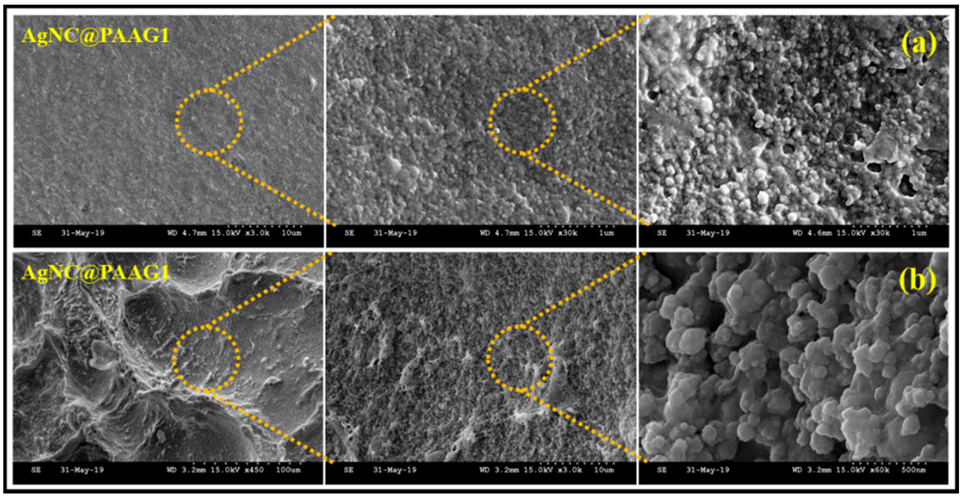

Figure 6. SEM morphology of guar gum based silver nanocomposite hydrogels (**a**) surface view of AgNC@PAAG1 (**b**) cross-sectional view of AgNC@PAAG1. (Scale = 100 µm, 10 µm and 500 nm, respectively, from left to right). Adopted from [155], with permission from Elsevier, 2020.

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 13.25×10^{-3} s^{-1} with conversion time within 1.5 min [127]. Manjari et al. documented the facile synthesis of SNPs using *Aglaia elaeagnoidea* flower extract. The authors mentioned the conversion time of PNP to PAP is around 15.0 with k_{app} value 22.5×10^{-2} min^{-1} [136]. IN contrast, the leaf extract of *Aglaia elaeagnoidea* 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 with 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 SNPs 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 2.38×10^{-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.

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