

Critical analysis of various supporting mediums employed for the incapacitation of silver nanomaterial for aniline and phenolic pollutants: A review

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Abstract—An enormous number of specific case studies have been reported that deal with the removal methodologies customarily employed for the reduction of common aqua-soluble pollutants [particularly nitrophenols (NPs) and nitroaniline (NAs)]. However, reviews that not only organize the literature in some presentable form but also work as a guideline for new scholars looking to exploit the field of nanocatalysis are surprisingly non-existent. Here in, an attempt has been made to comprehensively summarize the basic issues along with an insight to specific contributions devoted to NAs and NPs removal by utilizing the nanomaterial of silver. Furthermore, keeping in mind the significance of the surface functionalization of nanomaterial in catalysis, advantages/disadvantages of several entrapment mediums generally adopted for preventing the aggregation of nanomaterial are also summarized. A generalized overview of the various commonly employed removal practices along with its comparison to the catalytic reductive technique is also presented in the study. Finally, remaining unaddressed problems associated with this field and future directions for engineering cost-efficient and effective nanocatalyst assemblies are discussed in the end.

Keywords: Silver Nanoparticles, Nitroaniline, Nitrophenols, Catalytic Reduction, Review

INTRODUCTION

Nanotechnology/Nanosciences could, undoubtedly, be regarded among the most widely and extensively researched topics in the past three decades or so. This substantial attention is attributed to the exceptional and unique crystallographic features possessed by metallic nanomaterial when it is immobilized in its nanoform [1]. These features sets them apart not only from their bulk equivalents but also make them quite superior from the generally employed assemblies in various fields particularly in optics [2], biomedicine [3], catalysis [4], biotechnology [5] and tissue engineering [6] etc. For instance, numerous redox reactions, particularly reductive reactions, could be effectively performed while using the metallic gold nanoparticles, but its analogue (bulk metal) stays insensitive to these reactions and does not catalyzes them at all. This exquisite finding of Haruta [7] led to the advent of the new field of nanocatalysis, the phenomenal growth of which ears soon became very difficult to neglect [7]. Till date, an enormous amount of content could be found associated with this specific field and its trend is still going strong [8]. Metallic nanomaterial based catalysis is the buzz field and summarizing/organizing the available content into a meaningful form is a peculiar task that should be addressed with the same zealous interest as devoted to developing these nanocatalysts.

In terms of catalysis, the basic fundamental requirement that is considered the necessity for employing any particular substance as a catalyst is its high available and properly functionalized surface region, which could be exploited by reactants for lowering their

activation energy. When the metal is broken down into the nano-domain (specifically 1-100 nm), not only the amount of adsorption sites and surface area gets exponentially enhanced, but also the presence of some particular phenomena like surface plasmons resonance (SPR) and light entrapping ability (quantum confinement) further facilitate their usage as effective and economical catalysts [9]. Furthermore, additional benefits (such as reasonable catalyzing time, low employing concentrations, profligate kinetics in liquid phase, recyclable and easy separation from reaction media) of using these nanoassemblies have evidenced them to be far more suitable as compared to the traditional catalysts [10]. Up to now, the skill behind the synthesis and working of the nanomaterial has been largely understood, and abundant case studies which document the potential efficacious nanocatalytic systems could be easily found in the literature [11,12].

Silver and gold are generally exploited on a regular basis for the purpose of nanocatalysis [10,13]. The coinage metal of silver arguably holds quite a supreme position among the nanomaterials owing to its extensive historical significance in the various fields of human welfare [14]. Silver is generally utilized as a raw material/precursor substance in various industrial reagents, agrochemicals and pharmaceuticals etc. products production [15]. Furthermore, the biological applications associated with its antioxidant, antibacterial, antimicrobial, antifungal, anticancer, and anti-proliferating effects against lung cancer cells also encourage researchers to utilize this particular nanomaterial quite excessively [10,14,16,17]. Physical applications of silver nanomaterials include its usage as a saccharide biosensor, catalysis, biomedical therapeutics, electrochemical uses and optical applications [18,19]. Keeping in mind the aforementioned advantages along with the bonus benefits of cheapness, low cytotoxicity and high plasmonic sensitivity, silver nanoparticles (Ag-

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Np) were chosen as the main focal point in this review.

Expert study of these metal nanoparticles based catalytic assemblies would prove that this goal of nanocatalysis could only be achieved if the properties of the nanomaterial are effectively arrested in the nanodomain only and for that purpose; efficient entrapping medium (which not only prevents the aggregation tendencies of the nanoparticles but also does not influence its surface functionalization) are employed on a general basis [20,21]. Numerous methodologies for acquiring the stable and mono-dispersed nanoparticles have been utilized over the course of the years, which include capping agents, chelating ligands, inorganic and organic supports [22, 23]. Each of these supports exhibits peculiar characteristics and certain advantages/disadvantages which could be beneficial or detrimental in specific aspects. For example, rigid inorganic supports possess the major problem of non-biodegradability and recycling issues, while the organic supports, although addressing the degradability issue, are found to be not so reliable in terms of the long term incorporation as nanoparticles leakage issues are certainly always linked with these support beds [23-25]. Hence, for architecting an effective system for some particular application, the selection of a suitable support medium is of prime importance and should be done with certain amount of caution. Herein, an attempt has been made for summarizing the advantages/disadvantages of casually employed fabrication medium for Ag-Np in one place and certain impactful studies have been covered for developing a better understanding for the reader.

With respect to nanocatalysis, certain model reductions are generally performed after designing the system for investigating the catalytic efficacy of the prepared nanocatalysts. Catalytic transmutation of nitro-aromatic compounds into its more useful and beneficial form is probably the most used reaction in this regard. This popularity of these nitroaromatic conversions is due to the fact that these substances are regarded as non-biodegradable toxic aquatic pollutants and are particularly industrially removed from domestic/industrial effluents by employing lengthy post-water sanitation treatments taking days for completion [26,27]. Even after these procedures, acquired water was reported to be not entirely free from these pollutants [28]. Hence, developing the system that could not only perform the effective removal of these hazardous species but also could be potentially applied at commercial level is considered the need of the time and much effort has been invested in these specific conversions over the past years for achieving that aim.

This review article has been designed to specifically present an insight to the various supporting mediums generally utilized for obtaining Ag-Np entrapment for making nanocatalytic systems, which could be potentially employed for the reductive transmutations of the nitrophenol and nitroaniline compounds. To the best of our knowledge, no such review has been documented in the literature with these specifications. We will not only address the problem of organizing the literature, but also provide a guideline for any new researchers thinking of joining this field. Furthermore, we provide a spotlight on Ag-Np, nitroanilines (NAs) and nitrophenols (NPs) in terms of reviews as most of the reviews that are reported regarding pollutants and catalysis generally and surprisingly remain confined to gold nanoparticles and dyes [13,29-32]. Effort regarding reviewing these specifics, particularly nitroan-

iline and nitrophenol, does not even exist. However, few comprehensive studies regarding the nitroaromatic pollutants removal as a whole class are available in the literature [33-35]. Therefore, this study will prove quite beneficial for not only at industrial level but also to the multitude of interdisciplinary researchers looking for architecting ideal nanocatalytic assemblies.

In sections 2 and 3 of this review, the problem statement, nitrophenols and nitroaniline reductive conversion, is discussed and a comparative overview regarding customarily adopted removal methodologies is provided. In sections 4 and 5, a detailed analysis of Ag-Np mediated catalytic transmutation is reported and organization of literature is achieved by utilizing different stabilizing media as the basis of the classification. Section 6 covers the potential future predictions and directions that can be further studied and explored in terms of nanocatalysis.

NITROAROMATICS' IMPACT ON ENVIRONMENT

It is well-established that the rapid but unsustainable development obtained in the past century through opting industrialization/urbanization approach is generally acquired by the unplanned and excessive corruption of natural resources. Aquatic environment has received most of the deterioration in this regard as water is utilized in almost every chemical industry during synthesis, product finishing, and washing/purification etc. on a regular basis. Industries such as textile, cotton, pharmaceuticals, paints/dyes, paper and printing industries are the common industries that daily add various non-biodegradable inorganic pollutants into the natural aquifers through industrial waste effluents [36]. The sanitation/purification practices utilized for the wastewaters are not quite effective, and unfortunately a large amount of these water-soluble aromatics still remain at large in the water even after the conventionally employed post cleaning methodologies. With the release of this so-called cleaned water, these pollutants ultimately get accumulated into aquatic system posing a direct threat not only to the natural fauna and biota but also to the human life because of our high dependence over water for survival [37]. NAs [4-nitroaniline (4NA) and 2-nitroaniline (2NA)] and NPs [4-nitrophenol (4NP) and 2-nitrophenol (2-NP)] fall directly among the category of most common industrial pollutants habitually released into the environment.

Apart from the toxicology issues, these pollutants also prove to be resistant to the natural self-cleaning process of the environment. Hence, their non-biodegradability further results in prevailing other mutagenic and cancerous problems owing to bioaccumulation processes and made their removal extra difficult as compared to their organic biodegradable pollutants [38]. This non-degradability becomes further troublesome when humans further facilitate this particular property by coupling these synthetic products with substances like emulsifiers, block polymers, surfactants etc. These long-lasting hydrolysis and degradation proof products, which are specifically designed for acquiring various applications if not removed with extreme precaution eventually, become serious threats to the water consumers like us [39]. In this respect, highly efficient, effective and fairly green methodologies are required for addressing the problem of the nitroaromatic compounds.

Nitrophenols from industrial and agricultural waste are notorious because of their fairly high stability and water solubility. The U.S Environmental Protection Agency has listed them as potent pollutant as they not only generate odor concerns, but also are found to be explosive [40]. This character is due to the presence of the nitro group which has a strong inclination to withdraw the electrons. Successive nitro group substitution of aromatic compound results in more explosive products and the most common of it all is trinitrotoluene (TNT). Accumulation of this product in soil and water resources is essentially another environmental hazard owing to the considerable toxicity exhibited by this compound towards the living biota [41]. In terms of intoxication by any means may results in nausea, dizziness, cyanosis, headache, stomach ulcer and eye irritation [42]. Nitrophenols are the derivative of phenolic compound and are utilized excessively and regularly in the industrial sector (pharmaceutical, chemical, petrochemical, refineries, coal processing, and olive oil production) [43]. 2NP and 4NP are reported as toxic and recalcitrant chemicals exhibiting mutagenic effects also inducing chromosomal aberrations upon long term exposure [42].

NAs or benzenediamines are extremely reactive organic ecological pollutants produced in very large quantities as a consequence of anthropogenic activities. Literature available on quantization and quality tests performed over ground water and industrial effluents indicates that various scientists have reported the presence of an excess concentration of NAs in these water bodies [44-46]. This high concentration of NAs can also be attributed to the wide variety of its applications in the synthesis of dyes, pharmaceutical products, agrochemical materials and explosives. It is also employed as a precursor or starting material in the production of latex, pesticides, paints and medicinal drugs [47]. However, its extensive use also has its drawbacks. According to the Environmental Protection Agency, 2NA and 4NA have also been declared potentially carcinogenic and severely toxic pollutants as even in low concentrations they can cause mutagenic anomalies and disrupt life forms in the environment by causing chromosomal degeneration problems [27,42]. Hence, NAs and NPs require special attention in terms of removal considering the long-lasting detrimental tendencies of these compounds. General methods utilized for the removal of the NAs and NPs are detailed in the next section.

GENERAL REMOVAL METHODOLOGIES

Numerous physical as well as chemical methodologies have been adopted for the effective removal of NAs and NPs over the years. However, it was observed that traditionally the physical removal practices are more common on commercial scale rather than nano-materials. Fig. 1 summarizes the conventionally utilized removal practices for the NAs and NPs. Membrane-based separations of these substances include the use of several routes like microfiltration, reverse osmosis, ultrafiltration and nanofiltration for removal purposes [48]. Sawsan et al. [49] successfully achieved the 4NP extraction in the liquid media by using bulky, solid and hydrophobic ionic liquid membranes. Similarly, Zhang et al. [50] performed nanofiltration of 4NP by using composite membrane of Au/CNT. A comprehensive study regarding the membrane usage for sev-

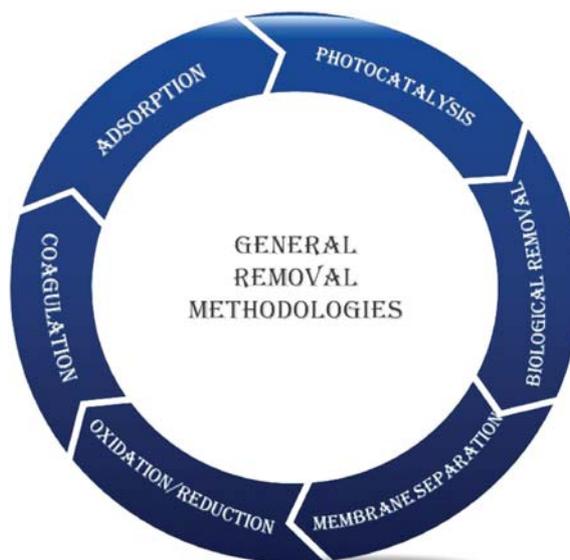


Fig. 1. General methods employed for reduction of NAs and NPs.

eral organic pollutants including 4NA, 4NP and several other pollutants has also been documented by Li et al. [51]. They utilized reverse osmosis and studied numerous membrane interfacial and fouling phenomena for each of the pollutants separately. But some basic universal problems associated with membranes like recurrent blockage, time consuming slow separation processes, membrane losses and designing of additional and costly filter cleaning setups with very high maintenance charges make the adaptation of these systems somewhat uneconomical [49,51]. Interestingly, even now whenever people report separation through membranes, the disadvantage of blockage and breaking of membranes is generally mentioned in the abstracts quite openly [49,52].

Moving on to the next methodology of biological mediated approaches, such as aerobic/anaerobic oxidation/reduction carried out with the help of microbes, the scientific community warmly welcomed these practices owing to the green and eco-friendlier features associated with them. Yet from an industrial point of view, profitable or economical application of this approach is also considered debatable because of the non-biodegradability problems accompanied with these pollutants. A comprehensive research carried by Bornick et al. [53] sheds light over some disadvantages that are always faced whenever the biodegradation techniques are applied over the aromatic pollutants. They intentionally spiked the aromatic pollutant concentrations in the samples acquired from River Elbe for investigating the biodegradability rates of these compounds. It was found that apart from considerable resistivity shown by the phenolic pollutants, NAs, explicitly 2NA, exhibited fairly high stability even in some quite drastic conditions. Surprisingly, simple aniline was easily reduced in aerobic conditions during the contact time of 3 h. But its nitro-derivative 2NA remained unaffected, exhibiting only 40% of degradability even after extreme exposure of 14 h [53]. Furthermore, most biological systems are selective and host-specific in nature and finding the system that could be universally employed for every aromatic species remained still a challenge that is needed to be answered [37,54]. It is also a com-

Table 1. Adsorption based removal of nitrophenols and nitroaniline

Analyte	Adsorbent	Notation	Discussion	References
2NA	Modified activated carbon (cotton stalk)	---	Relatively drastic conditions were used as optimum conditions and recovery test were not performed	[47]
4NA	Nanographene sheet	HSANGs	Adsorption/desorption efficiency with the optimum contact time of 5 min makes it quite economical catalyst	[62]
4NA	Bamboo charcoal	---	Economical and easy to prepare. However, separation of adsorbed content is not discussed	[63]
2NP	Modified activated carbon (Coconut-shell)	CSMA MCSAC	Greener approach however recovery rate was 48% and complete removal required nine cycles	[66]
2NP	Sedimentary phosphate	SP	High contact hours are required for effective removal	[67]
2NP 4NP	Fly ash	SACFA	Desorbing capacities were very low and equilibrium establishing time used for studies was quite high	[68]
4NP	Sawdust from acacia glauca	AGAC	Greener methodology with several predictors pointed out for further commercial use	[69]
4NP	Magnetic silica/graphene composite	Fe ₃ O ₄ @ SiO ₂ /GO	Removal of adsorbent from medium can be easily achieved but cytotoxicity and costs are not taken into account	[70]
4NA	Modified activated carbon (Camphor wood)	TCC	Impressive % removal of 90% yet desorption capacities have not been studied	[71]

paratively slow process as compared to others, which further decreases its chances of applicability [54].

Sedimentation (flocculation/coagulation) methodologies are also techniques frequently exploited for NAs and NPs removal. These technologies utilize lime, ferrous salts, alums, polyelectrolytes and bulky polymers during their operating procedures, which generates large amount of surplus waste/sludge in the reaction medium [37]. Ozbelge et al. [55] reported in-jar experimentation while employing four different coagulant substances for the effective separation of the phenolic compounds. Comprehensive literature collection regarding the use of this method could be found in the following reviews [56,57]. These procedures are not only lengthy but also require the development of supplementary operating/recycling apparatus for proper functioning. Disposal problems arising due to sludge further make their commercial use somewhat limited [37,55]. Moreover, orthodox physicochemical oxidative processes like Fenton's reagent exploitation or ozonization also drop short due to their non-economical draws such as the high cost and comparatively lower reduction rate [58].

Another important, and probably the most general approach, that is exploited for isolation of these pollutants is the adsorption technique. As shown by the technique name, adsorption depends on physical surface interactions between the pollutant and the system bed for the removal. Kumar et al. [59] reported the effectual removal of NPs (phenol and 4NP) by using the excellent surface functionalities of the activated carbon. Li et al. [60] utilized chitosan as the adsorbent for isolating the 4NP, phenol and chlorine-derivative of the phenol from the reaction medium. Allen et al. [61] documented complete kinetic analysis of the 2NP removal while utilizing the functionalized lignin as adsorbent. Similar studies could be found for the NAs regarding adsorbents [47,62-64]. Recent studies utilizing the adsorption phenomena are presented

in Table 1. However, certain limitations affiliated with this broadly used method further consolidate the dire need for developing effective systems for pollutant removal. In adsorption, the so-called removal of the pollutants is basically the successful transference of hazardous pollutant from one phase to another. Recovering the adsorbent for reuse purposes and the adsorbed pollutant retrieval for any potential application is relatively scarcely reported in literature. Furthermore, the recycling/regenerating methodologies required for the aforementioned work are costly and mostly ineffectual, which makes this usage method not only expensive but also problematic of sorts [39,65]. Chemical reduction by utilizing the nanomaterial is also another recognized technique currently employed for the effective removal of nitroaromatic compounds. Since it is related to the context of this review, it is discussed in detail in the next section.

NANOMATERIAL BASED CATALYTIC REDUCTION OF NPs AND NAs

Reducing organic pollutants into their less menacing and more industrially beneficial analogues is a well-organized practice which has been gaining exceptional popularity in the past three decades. Besides the general advantages (like high effectiveness, lower loading requirements, easy and clean dispensation processes), this technique surpasses the other techniques owing to its potentially vast commercial applicability applications. Several useful synthetic/industrial raw materials can be generated by carrying out these procedures. For instance, phenylethylamine produced as a consequence of NAs and NPs reduction has been given a clean slate by environmental agencies since it is only slightly harmful to humans causing only residual injuries upon acute ingestion [72]. These reductive products are also employed as precursors in the indus-

tries of pharmaceuticals, poultry, paint, antiseptic agents, dyes, antioxidants [73], polymers and as surfactants [74]. They are also further exploited as analytical tools in labs during the quantization and detection of aldehyde, carboxylic group and ketones [75]. Another edge that nanocatalysis provides is reducing the non-biodegradability of NAs and NPs. In some case studies, nanocatalysis of these persistent pollutants has led to the generation of biodegradable species which could also be utilized for the biologically mediated complete removal of these pollutants from the reaction medium [76,77].

Another factor that contributes in this vested interest in NAs and NPs by the researchers is that these reductive reactions are also generally utilized as a model reaction because of the ease with which the change in the reaction medium can not only be visually analyzed by the color changes but also can be experimentally scrutinized by spectrophotometric ways [27]. Nitrophenolate ions in NAs and NPs exhibit characteristic spike in the UV-Visible range whose length can be utilized as indicative of its current concentration in the medium [71,78]. Whenever NAs and NPs are reduced by the application of any reductant specie and catalyst, the length

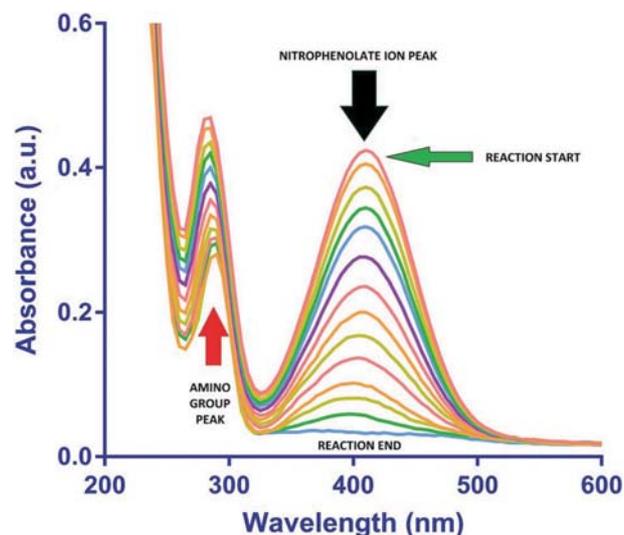


Fig. 2. UV-Visible spectrum of 2NA showing the progress of reaction through apparent decrease in the peak of the nitrophenolate ion.

Table 2. General employed nanomaterial for NAs and NPs reduction other than Ag-NPs

Nanocatalyst assembly					Reductive reaction of NPs or NAs				Reference
Metal	Immobilization support	Reductant	Particle size (nm)	Type of assembly	Analyte	Reductant	Solvent	Reaction parameters	
Au	Mono-trizole (1-trz)	NaBH ₄	---	Ligand stabilized suspension	4NP	NaBH ₄	Aqueous solution	Temp. 20 °C	[88]
	Bis-trizole (di-trz)		7.3±0.5						
	Polyethylene glycol (PEG)		8.3±0.5						
	Trz-PEG tail		3.1±0.3						
	Trz-hydrophobic PEG tail		2.9±0.3						
	Polyvinyl pyrrolidone (PVP)		2.2±0.4						
Au	CTAB@silica	NaBH ₄	15±2	Core-shell	4NP	NaBH ₄	Aqueous solution	Room temp.	[89]
Au	<i>T. terrestris</i> fruit extract	Fruit extract	7 & 55	Capped nanoparticles	4NA	NaBH ₄	Aqueous solution	Room temp.	[90]
Au	Brown algae	Brown algae	27-35	Capped nanoparticles	4NA	NaBH ₄	Aqueous solution	Room temp.	[91]
Pd-Ni	Aerosol OT	Hydrazine hydrate	10-28	Bimetallic assembly	4NP 2NP 3NP	NaBH ₄	Aqueous solution	Room temp.	[92]
Re	DNA strand	NaBH ₄	<1	Surfactant stabilized suspension	4NP	NaBH ₄	Aqueous solution	Room temp.	[93]
Ni	PVP & diethylene glycol (DEG) & dodecylamine (DDA)	Heating	80-200	Suspension	4NP	NaBH ₄	Aqueous solution	30 min heating	[94]
Fe ₃ O ₄ -MnO ₂	<i>P. frutescens</i> leaf extract	Leaf extract	5 nm	Nanocomposite	4NA	NaBH ₄	Aqueous solution	Room temp.	[95]
Pd	Polypyrrole & polystyrene	NaBH ₄	---	Hollow capsules	4NA	NaBH ₄	Aqueous solution	Stir & room temp.	[96]

of the peak starts reducing in accordance with the reduction rate that is going on in the medium. Consequently, when all the nitrophenolate ions available in the medium get reductively transmuted into amine group, it could be spectrally observed by the flat lining of its peak in the spectrum [79,80]. Furthermore, the amino group also actively interacts with UV-Vis rays and generates its own peak in the medium [81]. Moreover, the NPs and NAs give colored aqueous dispersions while their products impart colorlessness to the solution. Therefore, the color change further acts as a visual conformation of these reductive process [28]. Fig. 2 gives a generalized view of this process by spectrally presenting the 2NA reduction. Based on the reaction rates acquired by employing varying catalysts to these reactions, efficacy comparison among the catalyst can be achieved [82].

Moving on to the biggest problem that is currently found to be persistent in a wide range of literature is that the expensive noble metals like palladium, gold, platinum or zinc are preferably exploited for the purpose of nanocatalysis [83-88]. For eliminating this discrepancy of expensiveness, the main and focal nanomaterial that is elected for reviewing is the silver nanomaterial and only those case studies have been reported during the discussion of fabricating medium in the next medium, which has anything to do with this non-expensive metal of silver/Ag-Np. Table 2 covers some recent case studies that have been performed while using nanomaterial other than Ag-Np. Selection of a particular immobilization medium is another crucial factor that directly influences the efficacy of reduction of NPs and NAs. Nanomaterial, in general, holds extraordinarily high inclination towards instant agglomeration as it results in immediate lowering of their surface energy by providing thermodynamic steadiness [4]. Therefore, a fabrication/stabilization bed is an eminent requirement which should be carried out with extreme carefulness, because not only does a bad support hinder the reductive reaction by not fully surface functionalizing the nanomaterial, but also can be detrimental for the lifetime of catalyst if it is not fully stable itself [97-99]. For instance, bimetallic nanoparticles (BNp) assembly designed by Holden et al. [100] showed that Ag-Au BNp become aggregated easily on standing in the absence of the stabilizing agent and lose their catalytic ability. In the pres-

ence of the support, this BNp system showed up to 10-fold more effectiveness as compared to the reduction rate acquired by the simple mono-metallic nanoparticle system. Similarly, work done by Jiang et al. [101] further proves that without the silica facilitated immobilization of Ag-Np; these Ag-Np were found to be flocculating in the reaction medium. These circumstances can result in the regular and continuing loss of the selectivity and specificity of the catalysts [102].

Moreover, numerous organic as well as inorganic assemblies have been proposed for the entrapment of Ag-Np since the advent of the nanocatalysis. Few attempts regarding using Ag-Np without using any supporting substance in the medium have also been documented. Certain aggregation there reduces this thought into bits [103]. These studies further cemented the fact that a support bed is as vital for nanocatalysis as the nanomaterial itself and beforehand knowledge of advantages and drawbacks is vital information that every researcher should have before getting into this field of nanocatalysis. A large variety of reductants have also been reported which could be employed for carrying out the conversion of precursor salt Ag^+ ion into its Ag^0 nanoparticles. Sodium citrate [104], hydrazine [105], NaBH_4 [106,107], dextrose [108], formaldehyde [109], elemental hydrogen [110] and ethylene glycol [111] etc. are few examples of such material. However, the best results were generated by employing NaBH_{4V} which is the reason that most of the studies revolving around the reductive reactions utilize it in one way or another.

After establishing the basic idea regarding the nitroaromatic pollutants and the nanomaterials fundamental need of a supporting bed, the next section covers the types of assemblies that could be utilized in general for the Ag-NPs mediated NAs and NPs reduction. The various sorts of mediums are used for the purpose of categorization too, and explicit case studies with impactful and intriguing conclusions are presented here.

CASE STUDIES

1. Unsupported Ag-Np

Reports of such nature, i.e., case studies where stabilizers are not

Table 3. Unsupported Ag-NP for NAs and NPs reduction

Nanocatalyst assembly					Reductive reaction of NPs or NAs				Reference
Metal	Immobilization support	Reductant	Particle size (nm)	Type of assembly	Analyte	Reductant	Solvent	Reaction parameters	
Ag	---	H_2 gas	15-200	Suspension			---		[103]
Ag	---	H_2 gas	30	Suspension			---		[112]
Ag	---	H_2 , hydrazine, ascorbic acid, NaBH_4	7-15	Nanosuspension	4NP	NaBH_4	Aqueous solution	Low temp. dark place	[113]
					2NP				
					2NA				
Pd/Ag	---	Electrochemical replacement reactions	20	Bimetallic dispersion	4NP	NaBH_4	Aqueous solution	Room temp.	[114]
Au/Ag	---	Electrochemical replacement reaction	100	Bimetallic dispersion	4NP	NaBH_4	Aqueous solution	Room temp.	[115]

utilized at all for arresting the surface functionalization of Ag-Np, are quite scarce. Table 3 summarizes these particular reactions. Evanoff and Chumanov [103] designed support-free methodology for synthesizing Ag-Np. They used the flux of H₂ gas as a reductant and acquired relatively stable Ag-Np dispersion through centrifugation and filtering techniques. Solvating tendency of water molecules was accredited for the stabilization of the engineered Ag-Np. Anionic ion in H₂O (OH⁻) was proposed to get adsorbed on the Ag-Np, which provides the much needed surface stabilization to the forming Ag-Np in the medium [103]. This previous methodology was utilized by Merga et al. [112] in revised form and they succeeded in developing the Ag-Np with mean morphological size of 30 nm. They presented a clear picture regarding the shortcomings of the employed method and raised various questions on its practical application. Hydrogen flux effectiveness as a reductant was found debatable as the yield of Ag-Np in the reaction tub was quite low and most of the precursor was found to be still remaining in its oxidized form with no contribution towards the reaction at all. Heavy dependence of the preparative methodology further complicates things and adds one more additional parameter to consider during the processing. Redox process based catalysis was studied by them over prepared Ag-Np [112].

Attempts regarding the usage of the naked Ag-Np for the NAs and NPs reduction have also been stated. Pardhan et al. [113] performed reductive reaction of 4NP, 2NP and 4NA while employing the Ag-Np manufactured by utilizing the galvanic electrochemical replacement reactions. The engineered Ag-Np lacks stability and required particular conditions for optimum working such as low/cold temperature and completely dark storage place. Moreover, they exhibited strong affinity towards photolysis and susceptibility to oxygen upon interaction with air [113]. Reports regarding the preparation of bimetallic structures could also be easily found. Haung et al. [114,115] reported two such dendrite assemblies of Au/Ag and Pd/Ag nanoparticles for carrying out successful reduction of 4NP. Relative comparison of the two assemblies would indicate that high reductive rates were acquired by using Pd/Ag catalyst rather than the other. However, the important thing that could be deduced from these two studies is that not only preparative methodology is lengthy and difficult, but the excessive use of chemicals also results in the generation of large amounts of unwanted sludge containing surplus ions/salts (Cu²⁺, Cl⁻ and AgCl) generated in the various processing steps.

To conclude, the following key points could be summarized from the above discussion: a) rapid aggregation of the unsupported Ag-Np reduces its industrial applicability and adversely influence the catalyst life time [102], b) Support absence would mean that the engineered Ag-Np will have to be introduced into the sample in powdery form, which would result in its separation/recovery being quite difficult and uneconomical [98], c) the above-mentioned studies do not provide any information about recycling/reusing process of the catalysts, which raises various questions, and d) introduction of the un-trapped Ag-Np particles in the sample would increase the cytotoxicity issues associated with the leakage of nanoparticles in the reaction sample [116].

2. Surfactant/Ligand Based Stabilization

Various stabilizing agents that provided the much wanted stabil-

ity to Ag-Np by binding itself on the nanoparticle or forming stable chelating complexes have been utilized in the past years. In fact, if this approach was called the most pre-dated conventional practice utilized for stabilizing the nanomaterial, it would certainly not be wrong [117].

Application of suitable concentration of the capping agent in the medium is quite important as its large concentration impedes the accessibility of the reactant molecules towards the surface of Ag-Np, and therefore contributes in the declination of catalytic efficacy of nanocatalysts [118]. Mondal and Verma [119] used the process of bio-conjugation for generating the capping agent of EDTA (ethylenediaminetetraacetic acid) and tryptophan and then afterwards utilized it as a coating agent as well as a reductant for manufacturing Ag-Np in the range of 30 nm to 45 nm. Reduction of 4NP was achieved successfully, but the reduction rate was found to be not that much impressive (in comparison to latter studies given in section 5.3 and 5.4). Another study of particular importance was performed by Bastus et al. [120] who synthesized two types of capped Ag-Np and studied the effects of these coating species in the medium. Furthermore, they draw a comparison between the efficiency of two reductants (Tannic acid and citrate) that were utilized during the synthesis of Ag-Np. Their study elucidates that citrate coated Ag-Np surpassed in reductive reactions than Ag seeds covered with PVP as not only the coating agent of citrate exhibited less steric hindrance, but also the bulky polymeric configuration of PVP hinders the considerable diffusion of the reactants towards the metallic particle surface.

Various chelating ligands can also be utilized as the coating species. Recently, a multi-variant analysis of bi-functional (acidic as well as basic functionality in one molecule) acids as a chelating agent for the stabilization of Ag-Np was performed by Chadha et al. [121]. Ag-Np was prepared without using any reductant, which makes this study not only economical but also eco-friendly. But the harsh conditions, such as temperature of 80 °C and pH of 10, had to be maintained throughout the experiment for acquiring the Ag-Np. The trend observed with these chelating ligands also cemented the fact that when capping agents are used, the rate will be directly linked with the amount/number of the adsorption sites available to the reactant after the applied ligand has completely oriented itself around the nanoparticles. The more bulky the ligand, the more the space it will take and the less will be its 2NA reduction rate. Similarly, Eising et al. [122] synthesized several types of saccharide stabilized Ag-Np for 4NA reduction. The systematic kinetics was also studied for the reaction, and it was observed during the reduction mechanistic studies that overall reduction rate heavily depend upon the interaction of Ag-Np with reactants. Hence, that capping agent should be selected which does not blocks or tamper with the accessibility of the NAs or NPs to the Ag-Np.

Use of bimetallic or trimetallic assemblies have also been reported as reductive catalysts for nitro-organics. Ag-Np coupled with coinage metal of copper in the form of hollow spheres generated an increase in the reduction rate up to the approximate of two folds [123]. Similar studies with further improved results have been reported by Holder et al. [92], who utilized pluronic ligand as a stabilizer and engineered Ag-Au composites with excellent efficacy.

The 4NA reduction rate was enhanced up to approximately ten-fold than that of those generally employed monometallic assemblies. However, recovery processes were not discussed in this study. Moreover, thick layer of bulky polymer around catalyst could also generate diffusional barrier for the reactant.

Another important and most appreciated category which could be used for immobilization involves the bio extracts whose functional moieties exactly work in a similar way as that of the ligand stabilization. However, these assemblies lack durability and generate low yields. For instance, Khan et al. [124] performed the bio-synthetic process for the entrapment of Ag-Np. They utilized *Litchi chinensis* extract as the stabilizing as well as reducing agent. The reductive capacity of engineered assembly was investigating by using 4NA conversion as an exemplary reaction. Edison et al. [125] reported green preparation of Ag-Np by using green algae. Particular case studies associated with this biological method of synthesis for nanoparticles could be found in the following [126].

To summarize, although capping agents effectively fulfill the

purpose of stabilization for Ag-Np, their use will not be highly recommended when it comes to catalysis. Surfactants exhibiting strong chelating abilities such as EDTA, PVP, and PEG can reduce the catalytic efficacy of the system by causing steric hindrance against the reactants adsorption process over Ag-Np [127]. Additionally, regeneration or recovery of these highly stable dispersions from the reaction vile is also laborious and difficult. Even, ultra-centrifugation does not result in complete separation [128]. In this context, the inability of regeneration among these ligand stabilized nanomaterial could raise other cytotoxic as well as environmental concerns. Table 3 covers respective case studies [121,122,127,129-137] of such nature and presents a comprehensive overview of particular features associated with surfactant/ligand stabilized nanoparticles. Organic/inorganic supports discussed in next sections comprehensively deal with the issues discussed above.

3. Organic Polymeric Materials

With respect to organic substances, several two phase ionic liquids containing the water/solvent dispersed in the screens of flexi-

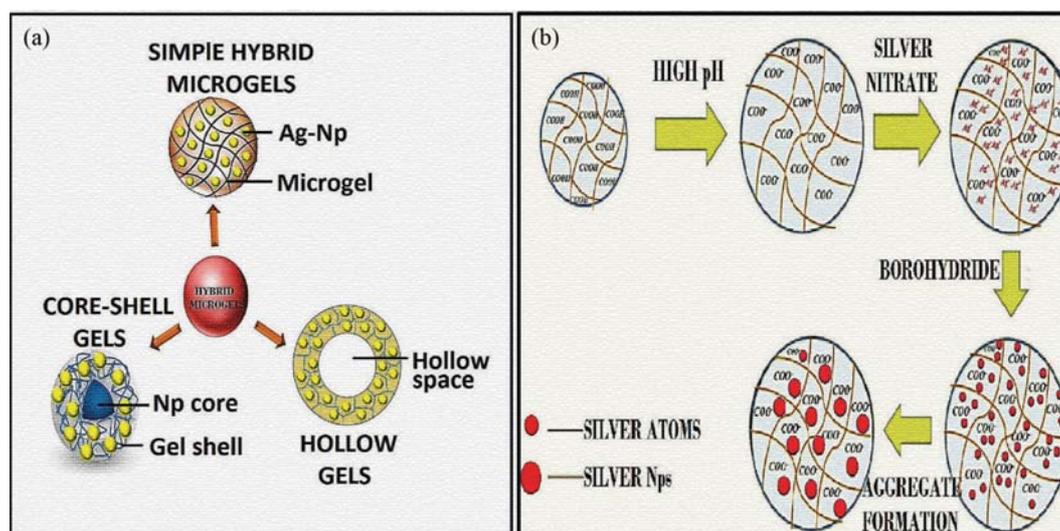


Fig. 3. (a) Various types of hydrogels employed for NAs and NPs reduction, (b) Nanoreactor process of the microgels resulting in the generation of immobilized Ag-Np by simply adding reductant and precursor salt in the medium (Adopted from our previous work, Najeeb et al., 2016 [27]).

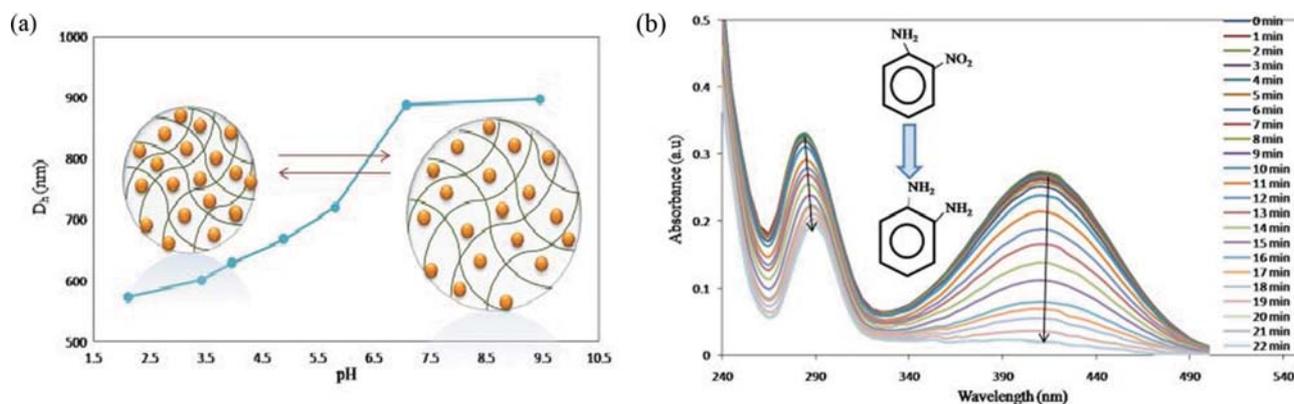


Fig. 4. (a) Variation in hydrodynamic diameter (D_h) of co-polymerized hybrid microgels in response to the change in pH of the medium (b) Catalytic degradation of 2-NA in the presence of hybrid microgels (Adopted from Farooqi et al., 2015 [78]).

Table 4. Surfactant/Ligand stabilized Ag-Np for NAs and NPs reduction

Nanocatalyst assembly					Reductive reaction of NPs or NAs				Reference
Metal	Immobilization support	Reductant	Particle size (nm)	Type of assembly	Analyte	Reductant	Solvent	Reaction parameters	
Ag	EDTA, TTHA, HEDTA, NTA	EDTA, TTHA, HEDTA, NTA	≈40	Dispersion	2NA	NaBH ₄	Aqueous solution	Stirring, temp. 25 °C	[121]
Ag	Sacchrides	NaBH ₄	3-8	Dispersion	4NP	NaBH ₄	Water and ethanol	Room temp.	[122]
Ag	PVP	NaBH ₄	≈6-9	Composites	4NP	NaBH ₄	Aqueous solution	Temp. 15 °C	[127]
Ag, Au, Co, Ni Pt, Pd, Ag-Pd, Ag-Pt, Ag-Au, Ag-Au-Pd	Glycerol	Hydrazine	2-50	Metallic nanosponges	4NP	NaBH ₄	Aqueous solution	Room temp.	[129]
Ag	EDTA	High temperature	100-800	Dispersion	4NP	NaBH ₄	Aqueous solution	Stirring, temp. 22 °C	[130]
Ag	Dextran	NaBH ₄	6.1 ± 1.3	Composite	4NP	NaBH ₄	Aqueous solution	Temp. 25 °C	[131]
Ag	Chitosan	Chitosan	5	Composite	4NP	NaBH ₄	Aqueous solution	Room temp.	[132]
Ag	PVP	Ascorbic acid	80-150	Nanosponge	4NP	NaBH ₄	Aqueous solution	Room temp.	[133]
Ag	Cyclodextrin	NaBH ₄	3.6-27	Dispersion	4NA	NaBH ₄	Aqueous solution	Room temp.	[134]
Ag	Cellulosic crystals	Cellulosic crystals	10-100	Nanocrystals	4NP	Cyclodextrin, NaBH ₄	Aqueous solution	Room temp.	[135]
Au-Ag	Pomegranate juice	Pomegranate juice	12	Core shell	4NP 3NP 2NP	NaBH ₄	Aqueous solution	Stirring, room temp.	[136]
Ag	<i>T. indica</i> extract	<i>T. indica</i> extract	30-50	Suspension	2NA 4NA	NaBH ₄	Aqueous solution	Room temp.	[137]

ble solid polymeric material called hydrogels/microgels are effectively employed for the reductive reactions of NAs and NPs [27]. Similarly, using polymers in the form of dendrites or block copolymers is another conventional way to acquire the same immobilization purpose for Ag-Np [138]. Microgels are a comparatively new approach in this respect. The sudden popularity gained by this class could be attributed to several factors: a) the synthesis process generally employed for its generation is not only cost effective but also rapid (particularly ionic and free-radical polymerization) [139]; b) Apart from providing the much needed support to Ag-Np, microgels can also be used as a nanoreactor (Fig. 3(b)) and generate the immobilized Ag-Np within its sieves [140]; c) Furthermore, these gels possess swelling/shrinkage aptitude in report of application of temperature, pH or other stimuli to the medium that could be utilized for dealing with the accessibility issues. Their open structure in swelled form is utilized by various researchers for NAs and NPs reduction [141]; and d) The sieve size of polymeric network can be used for manipulating the size of engineered Ag-Np [27]. Fig. 4 pictorially demonstrates the above mentioned properties in case of

typical co-polymerized microgels. Specific case studies with respect to organic material are presented in Table 5.

Use of *N*'-isopropylacrylamide [Nipam] gels is most common among the various sorts of gel available because the swelling/shrinkage temperature (Volume Phase Transition Temperature [VPTT], i.e., the temperature at which the change in the hydrodynamic radius of the microgels is maximum with respect to the temperature) of this gel is comparable with the human body, which in turn can also be used for targeted drug immobilization/delivery [141]. Lu et al. [142] reported catalytic gels assembly for 4NP removal. The Ag-Np was further modified by copolymer ligands for imparting more stability to it. Temperature values were found to be highly affecting the reduction rates. Another very interesting report documented by Shaoyang Li et al. [143] states the preparation of core-shell hydrogel system for the 4NP reduction. They first prepared Au rods and coated them with the Nipam gels. After that, Ag-Np was introduced into the gels by performing in-situ reductive reaction on precursor salt. The catalytic activity of this system was found to be strongly influenced by the laser irradiation. Xie et al.

Table 5. Organic material based Ag-Np for the NAs and NPs reduction

Nanocatalyst assembly					Reductive reaction of NPs or NAs				Reference
Metal	Immobilization support	Reductant	Particle size (nm)	Type of assembly	Analyte	Reductant	Solvent	Reaction parameters	
Ag	Poly *(Nipam)^(methacrylic acid)^(acrylamide)	NaBH ₄	---	Microgels	4NP	NaBH ₄	Aqueous solution	Temp. 25 °C and 55 °C	[11]
Ag	Poly *(Nipam)^(Acrylic acid)	NaBH ₄	40	Microgels	4NA	NaBH ₄	Aqueous solution	pH≥8, temp. 23 °C	[20]
Ag	Poly *(Nipam)^(allyl acetic acid)	NaBH ₄	20-40	Microgels	4NP 4NA	NaBH ₄	Aqueous solution	Temp. 27 °C	[26]
Ag	Poly *(Nipam)^(acrylamide)	NaBH ₄	10-20	Microgels	4NP	NaBH ₄	Aqueous solution	Temp. 32 °C	[72]
Ag	Poly *(Nipam)^(methacrylic acid)	NaBH ₄	---	Microgels	4NP	NaBH ₄	Aqueous solution	Temp. 23 °C	[81]
Au Ag	Nipam	NaBH ₄	6-10	Core shell gels	4NP	NaBH ₄	Aqueous solution	Laser illumination, room temp.	[143]
Ag	Poly (Nipam)	KBH ₄	≈10	Hollow microgels	4NP	KBH ₄	Aqueous solution	Room temp.	[144]
Ag, Au	Calcium alginate	UV-light	<10	Beaded microgels	4NP	NaBH ₄	Aqueous solution	Ambient conditions	[145]
Ag	Barium alginate	Irradiation	20	Beaded microgels	4NP	NaBH ₄	Aqueous solution	Ambient conditions	[146]
Ag	Polystyrene resins	Ice cold NaBH ₄	30±5	Resin composite	4NP	NaBH ₄	Aqueous solution	Room temp.	[149]
Ag	PEG methacrylate brushes	Citrate, NaBH ₄	7.5±2	Nano tree composites	4NP	NaBH ₄	Aqueous solution	Stirring, temp. 22 °C	[154]
Ag	Poly *(Nipam)^(acrylic acid)^(acrylamide)	NaBH ₄	20	Microgels	4NA	NaBH ₄	Aqueous solution	pH=9.14, temp. 22 °C	[155]
Ag	Amino dendrimers	NaBH ₄	5.6-7.5	Composites	4NP	NaBH ₄	Aqueous solution	Temp. 15 °C	[156]
Ag, Au	Poly *(Nipam)^(methacrylic acid)^(2-hydroxy ethyl methacrylate)	NaBH ₄	13	Hydrogel composite	4NP	NaBH ₄	Aqueous solution	Temp. 40 °C	[157]

Key of hydrogels notation: Poly [* (main monomer), ^ (co-monomers)]

[144] used hollow Nipam gels for the immobilization of Ag-Np. The free space present in the medium was beneficial for removing diffusional barrier for the reactants. Furthermore, 4NP reduction was also studied for the engineered system, which proves it to be highly thermally stable catalyst under drastic condition. These above discussed methods not only effectively fabricated Ag-Np, but also provided long-lasting stability by keeping them confined into polymeric sieves [72]. General kind of gels that are employed for NPs and NAs reduction are presented in Fig. 3(a), while Fig. 3(b) covers the basic mechanism behind in-situ production of Ag-Np inside the gels.

Using the beaded gels is another approach quite frequently adopted for NAs and NPs reduction. However, it has proven a little bit less effective than the gels discussed above. Saha et al. [145] used calcium-alginate based Ag-Np for the reduction of 4NP. Sim-

ilar methodology is also reported in case of barium-alginate [146]. The entrapped Ag-Np showed quite impressive results when tested for 4NP reduction. It was also witnessed that the presence of only Ag⁺ ion is enough for the onset of the gelation process, and stabilization of the engineered gels beads was achieved by the Ba²⁺ ions in the reaction. Nevertheless, it could also be seen from the reuse test performed in the same study that after only three usage cycles there was a sharp decline in the working efficiency of the nanocatalyst. This could be assumed to be happening because of the agglomeration of Ag-Np owing to the open structure of the gels that results in the loose confinement of Np in polymeric networks.

Organic dendrites fall in a way different category than that of gels when it comes to configuration and usage. Tree-like bulky polymeric structures serve the entrapment function quite efficiently, but reactant accessibility issues arise as a result. For instance, Rahid

et al. [147] used the modified ammonium dendrites for the Ag-Np fabrication and reported that branched dendrite exists over the Ag-Np as a monolayer and stabilizes it. Jana et al. [148] synthesized polystyrene resin bed for the fabrication of the Ag-Np and employed the assembly for the breakdown of 4NP pollutant. A multivariate report presented by Liu et al. [149] for the Ag-Np immobilization presents some quite interesting facts with respect to dendrites. They reported that increasing the content of the dendrite in the medium results in an increment in layer over layer deposition of dendrite over Ag-Np. Furthermore, this layered deposition adversely affects the reduction capacities of the catalyst, and pronounced decrease in the rates was observed with the increasing content of the dendrite [150].

Reports regarding the usage of organic matrix as a fabrication medium for Ag-Np are also documented. Yang et al. [151] synthesized Ag-Np while using the polymeric matrix of polyacrylonitrile (PAN). Although the 4NP reduction was achieved, the rate reported was quite low. This decline was ascribed to the nature of the support medium as the polymeric matrix contained cross-linked chains that were physically or chemically entangled with each other, resulting in the limited freedom available to the reactant for diffusion towards the catalyst. Therefore, rapid reduction was not possible with the use of this support. An attempt was made to remove this disadvantage by only utilizing the PAN nanofibers as the growing template for Ag-Np. Quite better results in terms of rates were acquired as compared to the previous one as the barrier was reduced in this case and easy interaction of reactant with catalyst was possible. However, the rate values still fell short of the rates that were utilized by using microgels and inorganic carbon nanotubes (discussed in next section) [152].

In summary, microgels/hydrogels were found to be the best suitable organic support as compared to the other competing supports of the same nature, owing to their open structure and durability [11]. These tunable gels cannot only be manipulated by simple external stimuli of radiation, pH and temperature, but also provide excellent hold over the size of the manufacturing Ag-Np. Easy recovery processes and the bio-degradability are also the handsome edges [153]. Dendrites, organic matrixes and beaded gelation although performs the immobilization effectively, but introduction of only optimum concentration of these is an absolute necessity and should be carefully determined beforehand. As too much concentration could result in the development of barriers in the diffusion practices of the reactant and will render the nanocatalyst ineffective [150,154].

4. Inorganic Supports

In the context of employing inorganic material for the fabrication of Ag-Np, graphene supports occupy a particular prestigious position among the materials of similar nature. This could be ascribed to the following facts: a) it contains comparatively free π -electrons owing to hybridization, and these carbon sheets can not only provide the storage place to electrons, but also can do the shuttling of the electron back and forth, which is ultimately utilized for reductive purposes by the NPs and NAs reactants [158]; b) furthermore, it is a 2-D material whose both sides are porous and could be utilized as a fabricating medium [159]; and c) the existence of oxygen moieties and other functional configuration

sites acts as binding sites and therefore, facilitates the conversion by speeding up the adsorption process of reactants over catalysts [160].

For these reasons, graphene is extensively employed as the medium for the reduction of NAs and NPs. Zhang et al. [161] followed the optical irradiation/photochemical route for generating highly uniform and monodispersed Ag-Np fabricated on the sheet of reduced graphene oxide (r-GO). Silver ammonia complex, i.e., $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ was used as precursor and stabilizing ligand in the reaction medium, while GO sheet served the purpose of support as well as reducing agent for the synthesis of Ag-Np. UV-Visible light irradiation initiated the in-situ reduction of the precursor by activating the electron-hole surface plasma of GO. Stored electrons in the GO electrostatically attracted the $[\text{Ag}(\text{NH}_3)_2]^+$ and converted it into silver atoms with the release of NH_3 . Atoms underwent aggregation for achieving the colloidal stability and generated Ag-Np of average size equal to 16 nm. For comparison, citrate-stabilized Ag-Np were also engineered and relative study was carried out for investigating the catalytic proficiency of the catalysts by doing 2NA reduction. The r-GO stabilized Ag-Np shows higher catalytic efficiency as compared to the citrate-stabilized Ag-Np up to 2.1-fold. Similarly, Yang et al. [162] developed Ag, Au and Pd nanoparticles of variant sizes by using ultra-sonication techniques and anchored them onto the partially reduced mat of graphene oxide (PRGO). No additional reductant was added in the medium. Instead, the partial reduction of the GO and adsorption of NPs on PRGO was obtained with lowering the temperature till 298 K and external application of pressure up to 100 kPa. The lowering in pressure also inhibited the oxidation of nanoparticles, which further improved the efficiency of the system. The sizes of the engineered particles were found to be 0.5-3 nm, 3-10 nm, and 1-20 nm for Pd, Ag and Au nanoparticles, respectively. Since the particle size of Pd was the smallest, highest catalytic activity was exhibited by them with Ag-Np following behind and Au coming at the last. Kinetics study and rate constant values for the reduction of 2NA, 4NA, 4NP and 2NP were also reported and elaborately discussed in the studies. Despite being integral factors for the validation of catalytic systems, the recyclability and reusability steps were not performed in the previous mentioned case studies.

From the above detailed discussion, one thing that could be clearly established in terms of synthetic procedures, organic material preparation is rather easier than that of the inorganic assemblies. But in terms of stability and withstanding the harsh conditions, inorganic supports are much better handlers than organic substances [154,162]. One very important notation that should be kept in mind is that till now we have only discussed those assemblies which are particularly using reduced graphene material. The pure or unmodified form of GO is not highly recommended for the immobilization. This is because the oxygen moieties in the sheets serving as nucleation sites can also electrically and optically interact with the fabricated nanomaterial rendering them unstable [163].

Aside from graphene, silicon dioxide (SiO_2) is another widely reported material that has been employed for studying NAs and NPs reduction. For example, sub-micron size of 100 nm was achieved by Zhou et al. [163] while using silver-mirror reaction for the production of Ag-Np immobilized on the sintered SiO_2 glass-filter

disks. The porosity and morphology of the disks were found to be directly influencing the density and size of Ag-Np. Catalyst-based reduction of nitroarenes was carried out for checking the efficiency of engineered assembly. However, a temperature of 50 °C was maintained throughout the whole experiment, implying the need of relatively harsh conditional requirement for the proper functioning of the catalyst. Dong et al. [164] and Le et al. [165] both utilized amino group functionalized SiO₂ support for stabilization of Ag-Nps. Fibrous and dendritic silica were generated by using hydrothermal and oil-water stratification method, respectively, which was later modified with organic moieties for better functioning. Li et al. achieved Ag-Np of the mean size of 4 nm by ultrasonically dispersing the dispersion containing modified fibrous nanosilica support in the presence of precursor metal salt. 4NP and 2NA were reduced by this catalyst. The approach of NH₂ functionalized dendritic SiO₂ as a support for anchoring Ag-NP was utilized by Dong et al. [164] This assembly provided relatively greater catalytic efficiency and recyclability than its fibrous counterpart and reduced 4-NA in the reaction time of 290 seconds with very high rate values. The enhanced stability and efficiency was attributed to the presence of an amino group that not only subdues aggregation but also prohibits Ostwald's ripening effect of NPs by firmly anchoring them to their places.

Similarly, using alumina for carrying out the reductive reactions is also quite common. Celen et al. [166] demonstrated a novel

route for developing highly disperse Ag-Np with a bio-inspired polymer coating and displaced them on the composite support of anodic aluminum oxide and polystyrene nanotubes. The catalyst carried out the reduction of 2-NA with a moderate apparent rate constant. The coating of a polymer of polydopamine provides an additional advantage of providing another redox relying on center other than Ag-Np, which aids in the conversion of 2NA. Another interesting thing to note here is that while organic mediums are mostly diverse and complicated, inorganic systems comparatively possess simple and identical symmetrical features in terms of structure and morphology. Most of the inorganic material supports utilize the organic moieties integrated into their systems one way or another as mentioned above. Suffice to say, combinational assemblies work better than isolated assemblies, as they have both their characteristics integrated into one system [58].

To conclude, in terms of inorganic materials, reduced graphene shows more superiority and more control over immobilization than others [167]. Furthermore, preparative methods employed for the modification purposes of inorganic materials are quite lengthy and time-consuming [166]. Similarly, size and density dependence of forming NPs over the porosity of the inorganic medium is also problematic. Reduction in pore size enhances the number of fabricated nanoparticles, but in turn also increases the diffusion time required by the reactant to get adsorbed over the NPs. Also, aggregation of the NPs was also observed in highly porous inorganic

Table 6. Inorganic material based Ag-Np for the NAs and NPs reduction

Metal	Nanocatalyst assembly				Reductive reaction of NPs or NAs				Reference
	Immobilization support	Reductant	Particle size (nm)	Type of assembly	Analyte	Reductant	Solvent	Reaction parameters	
Ag	r-GO, secondary amine ligands	r-GO	16	Nanocomposites	2NA	NaBH ₄	Aqueous solution	Ambient conditions	[161]
Ag, Au, Pt, Pd	r-GO	Acidic zinc solution	--	Hybrid sheets	4NP	NaBH ₄	Aqueous solution	Room temp.	[168]
Ag, Bi	GO, Bi ₂ O ₃	Thermal heating	2-70	Nano sheets	4NP	NaBH ₄	Aqueous solution	Temp. 0 °C	[169]
Ag	SiO ₂ , organic copolymer	Co-polymeric moieties	14	Nanosphere assembly	4NP	NaBH ₄	Aqueous solution	Room temp.	[170]
Ag@Pd	Functionalized Fe ₂ O ₃ , PVP, diamines	Ethylene glycol	6.9±1.3	Core-shell assembly	4NP	NaBH ₄	Aqueous solution	Room temp.	[171]
Ag	SiO ₂ , CTAB	Ascorbic acids	9 (core)	Core-shell assembly	4NP	NaBH ₄	Aqueous solution	Temp. (20-90 °C)	[172]
Ag	SiO ₂ , CTAB, poly-ethyleneamine	NaBH ₄	4	Core-shell assembly	4NP	NaBH ₄	Aqueous solution	Room temp.	[173]
Ag	Organic dendrites	PVP, reflux and stirring at 70 °C	11.6±0.2	Nanohybrids	4NP	NaBH ₄	Aqueous solution	Room temp.	[174]
Ag	GO, organic matrix	NaBH ₄	10	Nanosheets	4NP	NaBH ₄	Aqueous solution	Stir, room temp.	[175]
Ag	Graphene hydrogels, dextrose	NaBH ₄	10-20	Nanocomposites	4NP	NaBH ₄	Aqueous solution	pH 10.5, Room temp.	[176]

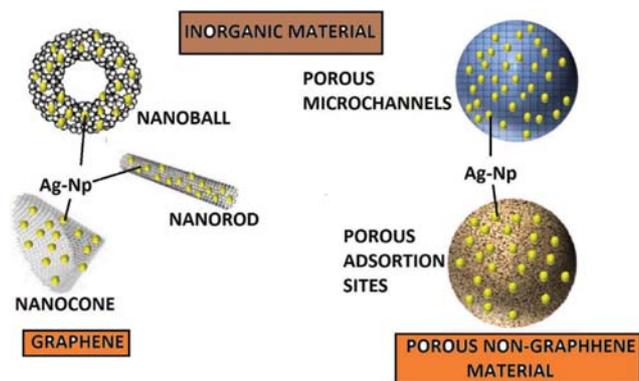


Fig. 5. Various types of the inorganic material employed for the NAs and NPs reduction.

material owing to Ostwald's ripening effect [164]. However, if the reaction medium is prone to harsh conditions, then inorganic mediums are the best mediums in terms of tensile strength [167]. Similarly, leakage problems of nanomaterials from the organic supports could be effectively eradicated by using the following supports [58]. Table 6 summarizes the basic inorganic materials employed for the NAs and NPs reduction and Fig. 5 presents the general assemblies of these supports.

REMARKS AND FUTURE DIRECTIONS

a) The main observation that could be drawn from the above literature is that most people focus on developing nanocatalysts by employing only one type of material as a support. Integration/mixing of materials should be done to generate heterogeneous assemblies containing the beneficial aspects of both the materials in one system (Tables 2-6).

b) Absence of durability tests in most studies is a persistent problem that was faced while doing the literature study for any kind of the fabrication medium used. Furthermore, most of the catalytic tests were performed right after the synthesis of catalysts and at room temperature. Effects of environmental factors/harsh condition over the functioning of catalyst are hardly reported (Tables 2-6). Recycling practices and stable catalyst generation that could handle storage issues at the industrial level are the two important factors that should always be considered when proposing the future application of nanocatalysts.

c) Although impressive efforts have been reported in terms of nanocatalysis, designing the catalyst exhibiting both effectual catalytic efficacy and commendable durability at the same time is still a milestone that is needed to be achieved for the commercialization of the nanocatalysts. Most studies focus on only one aspect, and generally the latter is sacrificed for acquiring the first. Hence, developing the catalyst that would not compromise any of the above two traits is highly desirable and this area is worth exploiting by all means.

d) Another factor that is comparable in nature with the point (a) explained above is that in terms of silver, the bimetallic or trimetallic assemblies are surprisingly very scarce (Tables 3-6). Few systems that are found to be reported clearly indicate that these assemblies possess superior catalytic capabilities than that of the

monometallic system. Therefore, focus should be given to the preparation of bimetallic assemblies (comprising of non-expensive metals) in terms of engineering effective nanocatalysts.

e) With respect to the insights about the applied supports, organic material shines out not only in terms of bio-degradability, but also because of the ease with which they can be prepared. Inorganic materials mostly require harsh environment for the synthesis. This also provides an edge in that they can withstand the environmental factors more efficiently than that of the organic material. Hence, amalgams or hybrids of these two assemblies could be prepared for acquiring the structurally sound effective nanocatalysts, and efforts should be invested in developing more economical prototype systems that could be practically/industrially applied on a large scale reduction.

f) Most of the reports whether in the organic/inorganic section indicate that generally quite attractive and colorful grafting assemblies have been reported as the fabrication beds (Fig. 3 and 4). However, these nanoassemblies, whether how beautiful they look in appearance could generate serious toxic hazards if not handled properly. So, instead of investing so much interest in these supports, attention should be given to greener supports like clay, soil etc. and improvements should be made there too for converting them into suitable as well as sustainable catalysts.

CONCLUSION

In this review, we have attempted to comprehensively and systematically summarize the contributions on the removal of anilines and phenolic pollutants by using silver nanomaterial. These studies were categorized on the basis of the employed immobilization bed, and the characteristic features (advantages/drawbacks) were also studied in comparison to each other for drawing the overall picture with respect to supports. Moreover, detailed analysis of the pros and cons of the other methodologies customarily employed for the removal in comparison to catalytic transmutation approach are also presented in the study. Spotlight has been given to gels and graphene in terms of explanation as these two materials are the most extensively utilized systems in their respective categories. While doing literature surveys, hidden issues that are not generally discussed while reporting the nanoassemblies are brought into light. Furthermore, the remaining persistent problems are also summarized at the end for the easiness of the reader. Consequently, this review presents a comprehensive guideline to the new researchers not only in terms of methods but also the type of material to be used when working on designing novel, economical and effective nanocatalyst systems.

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