




Elimination of dyes by catalytic reduction in the absence of light: A review

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ABSTRACT

Developing novel technologies for the effectual treatment of wastewater comprising contaminated organic pollutants is of extraordinary importance across the globe. In the last few years, removal of organic pollutants using various nanocatalysts from aqueous solution by chemical reduction in the presence of NaBH₄, as a reducing agent, has become an established route. Nanomaterials show great potential for the improvement of water treatment technologies. Recently, catalytic reduction of dyes by using various nanoparticles has received significant attention due to their effectiveness in degradation and producing less toxic and environmentally benign products. Herein, this comprehensive review discusses the classification of nanocatalysts, mechanisms involved in catalytic degradation of various types of dyes, recyclability of nanocatalysts and characterization techniques for various nanocomposites. We aim to review and summarize the recently published literature and R&D progress in catalytic reduction of various water pollutants. Different nanocatalytic assemblies used for reduction of dyes and their division based on nature of nanoparticles and composition of supporting materials have been described critically. A mechanism for chemical reduction of nitrophenols, methylene blue, Congo red, and methyl orange in the presence of nanocatalysts has been elaborated in this study.

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Introduction

Rapid industrialization in recent years has been primarily considered as one of the main causes of the humungous increase in environmental concerns including air, soil, and water pollution [1, 2]. Various environmental factors pose huge impact on quality of life particularly water pollution. The chemicals added to the groundwater reservoirs owing to the working, processing, purification processes of the various industries are causing serious health problems in human beings. Water pollution is caused by addition of various hazardous materials released from different industries and has been considered a major health problem around the globe, especially in developing countries. Keeping in view high population growth along with stringent health-based regulations and economic development, there is more demand for high-quality water (i.e., water that is free of toxic chemicals and pathogens) [3–5]. The need for freshwater is of utmost importance for life on earth and its reservoirs are effecting by chemical discharge from industries and agricultural resources as well [6, 7]. The addition of hazardous chemicals in freshwater is attributed to two sources (i) geological, (ii) anthropogenic (i.e., man-made) [8]. The hazardous or toxic materials affecting the quality of water include various dyes, compounds like fertilizers, insecticides, chemical species, heavy metals like Hg, Cu, Cr, Pb, synthetic detergents, oils, solvents, disinfectants, pool chemicals, etc. [9, 10]. So the removal or degradation of hazardous materials and contaminants from wastewater, ground, and surface water is a significant global challenge. Various methods and techniques have been reported for water purification including sedimentation approach, distillation, different chemical methods like coagulation, precipitation, and use of adsorbents, filtration, etc. [11–16], where oxidation processes have gained much attention owing to their efficiency.

Dyes are the major source of dangerous contaminants discharged from different companies, such as the paper, textile, paints, cosmetic, printing, food, pulp, and pharmaceutical industries [17–22]. Keeping in view the tendency of toxic chemicals and dyes to cause skin problems, coughing, dyspnea, eye irritation, liver and kidney damage, lung disease, ulcers, respiratory problems, and cancer, there is utmost need to improve water quality by removing these

hazardous materials [23–26]. Thus, removal/degradation of toxic chemicals from wastewater is a foremost global challenge because of their potential toxicity, carcinogenic and teratogenic properties toward plants, animals, and humans [27–30]. Dyes can easily adsorb/reflect sunlight, slow down photosynthesis, and effect aquatic plants in an ecological system [31, 32]. In addition, they are constant threat to natural environment due to low biodegradability; accumulate in natural environment as persistent pollutant. Classification of dyes depends on their basic skeleton or structure, their source, and nature of fiber (i.e., most compatible). They are categorized as, acidic, basic, anthraquinone, azo, and metal complexes [32–35].

Various sanitization methods have been reported in literature [13, 14, 36–38] such as oxidation processes (chemical, biological, or physical), catalysis [39], photocatalysis [40–43], biological treatment, coagulation, membrane systems, ozonation [24, 44–50], anodic oxidation [51], catalytic wet air oxidation process [52, 53], chemical reduction [54], electrochemical methods [55–57], hydrogenation [58, 59], microbial degradation [60], adsorption [61, 62], Fenton process [63], and so on. These dyes are very resistant and difficult to decompose using conventional methods. Therefore, different approaches are made to minimize the absorption of pollutants into the environment for instance: chemical sedimentation, ion exchange, solvent extraction, evaporation, oxidation, electrochemical treatment, membrane separation, membrane bioreactors, incineration, and absorption [64, 65]. All of these approaches have short comings like incomplete mineralization, chemical consumption, disposal of dense solution, laboratory scale, pH dependence, high consumption of energy, high material costs, sludge treatment, etc. [66, 67]. So, there is dire need to develop new technology for efficient removal of the dyes from the environment.

Among these approaches, chemical reduction has attained great attention because of its high efficiency, easy operation, and low cost. In this approach, dyes are converted into less toxic materials that can be further degraded before release [70–78]. Chemical reduction of several dyes by sodium borohydride (NaBH_4) as the reducing agent is an economic, safe, highly efficiency, and green alternative approach. Hence, catalytic degradation by NaBH_4 is superior to other traditional methods in terms of less time-

consuming, simple design, easy operation, and their recyclability is the main motivation to choose this method for review [79–84]. However, this process is thermodynamically favorable and kinetically unfavorable in the absence of a catalyst [70–73]. So, different catalytic system has received considerable attention for variety of applications in several fields as they exhibited tunable physicochemical properties [85–90]. Bimetallic catalysts possess better catalytic potential as compared to their individual metal (monometallic analogues) owing to synergistic effects between two metals and degree of freedom that can be adjusted to increase the catalytic efficiency of bimetallic nanomaterials [91–95]. For instance, Mei et al. recently reported the efficient degradation of organic dyes (MO, RhB, and Rh6G) over an organic–inorganic bimetallic catalysts P(St-co-AAM)/PGMA in the presence of NaBH₄ reducing agent. The uniform distribution and popcorn like geometry of the prepared catalysts resulted in complete degradation of these dyes within two minutes of working [96]. Moreover, the constituents of bimetallic catalytic system play significant role in reaction and provide a suitable environment for the catalytic performance [97–102]. In majority of cases, metal and metal oxide nanomaterials are employed as redox mediator-RM to enhance the degradation rates of electron-accepting priority pollutants [84, 103–107]. Indeed, redox mediators consist of a redox couple accompanied with a high electron transfer rate, which stimulates the interaction between an electron donor (NaBH₄) and electron acceptor (dyes) species by acting as an electron shuttle [82, 105, 108–111]. Pereira et al. demonstrated the effects of thermal treatment on the performance of activated carbon as redox mediator for the degradation of various azo dyes including Direct Blue 71, Reactive Red 2, and Acid Orange 7. The enhancement in surface morphology of activated carbon upon thermal treatment and pH of the medium were reported to be the key factors in the effective degradation of dyes [112]. The transfer of electrons is an important step because a high potential difference between the electron donor and acceptor can hamper electron transfer. Therefore, an effective catalyst with an intermediate redox potential can act as an electron relay to assist electron transfer [70–73, 113]. Several redox mediators have been employed as catalysts to increase the reductive biotransformation of electron-accepting contaminants [114–121].

Nanotechnology is vital for advancement of various technologies and industrial sectors, particularly environmental sciences, material sciences, energy, information technology, biotechnology, food safety, biomedical sciences, biochips, memory devices, and biosensors. The role of nanotechnology for current development and progress in biotechnology, chemistry, physics, and material sciences is well documented involving design of nanostructures with unique characteristics [122–124]. Nanotechnology has attracted scientists around the globe owing to its vast applicability and enables researcher to devise novel strategies for designing, synthesis, and characterization of various nanomaterials with unique characteristics. Nanoparticles being small-sized with significantly improved crystallographic characteristics are of paramount interest in various fields of science. Various surface-dependent applications of nanomaterials are attributed to their exceptionally high surface available for interaction. For instance, heterogeneous catalysis represents one such research approach with wide applications in environmental remediation [118, 125–128].

Nanomaterial has a main catalytic domain for reaction of reacting species while stabilizing medium serve to immobilize NP or nanomaterial. Nanoparticles deserve a key position among various types of reported nanomaterials with size range 1–100 nm and a high surface: volume ratio [129]. The optical and electromagnetic characteristics of nanoparticles are attributed to high coupling constant among electromagnetic radiations that lead to surface plasmon resonance (SPR) phenomenon. Compatibility of NP's size and electromagnetic radiations lead to strong coupling between them [130–132]. Various types of NPs have been reported in the literature, namely organic and inorganic NPs, metal, and metal oxide NPs, and TM-doped NPs. A very recent study on the biosynthesis of silver NPs was reported by David and Moldovan where they utilized *Viburnum opulus L* extract as a bioactive source to degrade organic dyes. Highly stable and reducing Ag NPs effectively degraded the Brilliant Blue FCF dye in water [133].

. Although catalytic potential of nanomaterials depends on surface area of nanoparticles still stabilizing medium plays a key role to finalize surface area of NPs [134–137]. In addition, agglomeration tendency of NPs presents a major issue during synthesis of NPs due to high energy caused by dangling bonds

present at their surface. Hence, self-assembly and aggregation facilitate in lowering of surface energy of NPs but decreases surface area of NPs and reduces their applications in various fields. Using stabilizing medium for fabrication of NPs helps to cope with this problem of self-agglomeration and keep size of NPs in desired range [43, 138]. For instance, Joseph and Mathew utilized starch as a stabilizing agent to fabricate Ag NPs via microwave-assisted approach for the degradation of MO and RhB dyes in the presence of NaBH_4 . Spherical Ag NPs with uniform size were produced in the presence of stabilizing agent which opened new insights in to the commercial fabrication of nanocatalysts [139]. Various characteristics of stabilizing agents including enhanced chemical and thermal stability alongside small density values contribute toward catalytic potential of synthesized NPs, reduce Ostwald ripening tendency, and increase their stability [140, 141]. Keeping in view the significance of various nanocomposite materials for degradation and reduction of hazardous chemicals and dyes here, a detailed review of literature providing information about classification of nanocatalysts, mechanisms involved in catalytic degradation of various types of dyes, and characterization techniques for various nanocomposites is provided.

Classification of catalytic systems

Both nature of synthesized nanoparticles and stabilizing material for any given nanomaterial assembly provide basis for classification of catalytic systems. Following two classification criteria have been reported.

Nature of nanoparticle

Recently, metal nanoparticles have been extensively employed for catalytic degradation of pollutants and organic dyes. Keeping in view, the unique surface properties and chemistry along with small reduction potential values, the metal nanoparticles have been regarded as an attractive catalytic system for various electron transfer reactions. Two categories specified for metal nanoparticles based on their building block's nature are: (i) monometallic NPs and (ii) bimetallic NPs.

(i) Monometallic metal NPs

Nanoparticles made up of regular array of building blocks of same metal are characterized as monometallic nanoparticles. For instance, silver (Ag), nickel (Ni), gold (Au), copper (Cu), cobalt (Co), etc., have been employed as catalytic systems with potential to catalyze isomeric aromatic nitro phenols [142, 143]. Silver (Ag) NPs being eco-friendly and cost-effective have been used for the catalytic reduction of 2-NP and 4-NP. Various types of stabilizing systems have been reported for nanoparticle fabrication [142, 144–151], like reduction of nitrophenols is achieved successfully using Ag NPs immobilized on microgel. An interesting fact related to use of microgel as a stabilizing medium is its dispersed phase that is water in nature providing an efficient working atmosphere for reduction of 2-NP and 4-NP. Also, changes in the mesh size microgels can facilitate to control and manipulate the size of nanoparticles of interest. Variation in temperature along with other reaction conditions has a major contribution to effect catalytic potential of a given system [134, 142, 145, 147, 151, 152]. Similarly, green synthesis of Au nanoparticles using *Breynia rhamnoides* plant extract as the stabilizing medium and as reductant is reported by Gangula et al. The stabilization potential of plant extract is attributed to presence of various bioactive constituents like aromatic and phenolic compounds [153]. Although given synthetic approach was quite eco-friendly, simple, and more facile still its characteristic properties were not comparable to NPs synthesized through simple chemical methods. Later, Zayed and Eisa reported same methodology for synthesis of Au NPs using *Phoenix dactylifera* plant extract as capping agent [154]. Similarly, Guria et al. utilized cultural filtrate *Fusarium MMT1* strain for synthesis of protein-stabilized nano-gold particles and used them for reduction of 2-NP and 4-NP [155]. Even though Au nanoparticles have wide applications and unique characteristics still it has limited applications at an industrial scale due to their high cost, as a basic requirement of water purification plants and industries is to provide services at a lower cost. In addition, Ni NPs represent another type of monometallic NPs that have been employed for reduction of 2-NP and 4-NP. For instance, Sahiner et al. reported synthesis of Ni NPs using in situ reduction technique and immobilized on hydrogel system [156]. They reported efficient degradation capacity of Ni NPs

immobilized on hydrogel, i.e., poly (2-acrylamido-2-methyl-1-propanesulfonic acid) [p(AMPS)] for 4-NP using sodium borohydride (NaBH_4) acting as a reducing agent. Another important feature related to reduction of dyes by NPs system is involvement of stabilizing medium to facilitate electron transfer reaction between reductant and dye. Examples for these systems include usage of graphene, GO, or reduced graphene (RGO) as medium for immobilization of NPs. Jebaranjitham et al. utilized Hummer's method for production of two types of amino-functionalized graphene oxide and compared their efficiency for nucleation as well as stabilization of Ag nanoparticles. They reported better dispersion potential of alkyl-diamine-functionalized GO for Ag nanoparticles that did not agglomerate in polar solvent [157].

(ii) Bimetallic NPs

Bimetallic nanoparticles have huge significance and have attracted attention of scientists around the globe being better in catalytic performances as compared to the monometallic nanoparticles [158]. Bimetallic nanoparticles are heterogeneous, i.e., composed of different types of metals that enhance their tendency to assemble during synthesis or fabrication. The better efficacy and superior nature of bimetallic nanoparticles are attributed to the combined characteristics of both metals in a given system. The stability, catalytic potential, resistance toward poisoning or degradation, and selectivity features of bimetallic NPs are much better than monometallic NPs [159, 160]. For instance, Ghosh et al. reported better and even more significant performance of bimetallic Pt-Ni nanoparticles for reduction of 4-NP as monometallic Pt NPs investigated under same reaction conditions [161]. Similarly, using core-shell Ag@Pt b-MNPs immobilized on sepiolite nanofibers for reduction of 4-NP showed better catalytic performance as compared to Ag/sepiolite or Pt/sepiolite alone as reported by Ma et al. [162]. Later, Lu et al. [58] reported in situ synthesis of bimetallic Au-Pt NRs supported on core-shell microgel to avoid aggregation of synthesized NPs. The better catalytic potential of Au-Pt NRs for degradation of 4-NP is accomplished due to combined effects of characteristics of both Pt and Au metals in single nano-system [163]. Catalytic potential of any given bimetallic NP assembly is dependent on compatibility of both metals as suggested by Pozun et al. who synthesized different alloys of bimetallic nanomaterials like

Pt/copper, palladium (Pd)/Cu, Pd/Au, Pt/Au, and Au/Cu stabilized on G6-OH poly (amidoamine) [PAMAM] dendrimers. They reported Pt/Cu as most efficient nanoparticle system for reduction of 4-NP owing to strong binding tendency of both metals [91], while Au-Ag b-MNPs stabilized on graphene oxide also showed better catalytic performance for reduction of 4-NP as compared to GO-supported monometallic Au and Ag NPs [164]. Furthermore, bimetallic nanowires like Cu@Ni nanowires synthesized through facile liquid-phase reduction technique and graphene as supporting medium has shown enhanced stability along with better catalytic efficiency for 4-NP reduction. Although various multimetallic NPs systems have also been reported very limited literature has been reported in this regard [165]. An example of such multimetallic system was reported by Gao et al. who employed liquid-phase reduction technique for synthesis of multi alloy system comprises of Pd, Ni, and phosphorous (P)[PdNiP/ RGO] catalyst having high stability and catalytic tendency. This higher catalytic potential and performance of multimetallic NPs system is attributed to well distribution of alloy on the surface of RGO [166].

In summary, metal NPs have shown good potential for the catalytic degradation of organic pollutants in wastewater owing to their unique features like small reduction potentials and superior surface chemistry. Although monometallic catalyst have shown great results in the degradation of various organic pollutants such as nitrophenols, another class of catalytic systems named bimetallic nanocatalysts have received much attention lately. This is due the superior stability, chemical potential, and selectivity of bimetallic systems over the traditional monometallic nanocatalysts. Furthermore, the synergism between the two compatible metal components can provide us with a better degradation mechanism which is long lasting as well. However, the traditional synthetic routes for the fabrication of these metallic systems are not environmental friendly and highly costly. Therefore, researchers have diverted their attention to look for environmentally benign fabrication routes like green synthesis and significant developments are being made in this regard.

Stabilizing medium

The surface area of MNPs plays an important part in the catalytic reduction of dyes that is secured by using various stabilization agents including polymers, non-polymers, organic-inorganic compounds, and biogenic compounds. To ensure a better surface morphology, use of various stabilizing agent to fabricate NPs with superior surface properties has become inevitable. Following are some of the conventional stabilizing mediums adopted by the researchers for metal NPS fabrication in the past few years.

Polymers as stabilizing agents

Polymers have been extensively employed for improving properties of various materials particularly their surface characteristics. Previously reported polymer systems employed to enhance stability of metal NPs are dendrimers, polymeric matrix, hydrogels, core-shell or yolk-shell systems that serve as capping agent to perform catalytic activity [167–183]. For instance, dendrimer utilizes steric repulsion while polyelectrolytes involve electrostatic repulsion to fabricate nanoparticles. Dendrimers being neutral have various advantages as compared to polyelectrolytes. Similarly, both homopolymeric and hetero polymeric matrices have been used as capping agent in case of simple polymeric systems. In addition, various polymer matrices have been reported to stabilize and synthesize metal NPs [184], i.e., polystyrene [185], polyvinyl pyridine [186], polydopamine [186], polyvinyl pyrrolidone [187], polyacrylic acid [188], or block copolymer like poly(ethylene oxide)-poly(acrylic acid) [189]. Water-insoluble polymer matrices have been employed for synthesis of NPs with desired shape and size that are easily extracted from medium. For instance, polystyrene-polyvinyl pyridine (PS-PVP) beads have been utilized for synthesis and stabilization of Ag and Ru NPs [185]. Hydrogels represent another important stabilizing agent used for synthesis of metal nanoparticles whose characteristic like change in volume with stimuli alongside electronic, catalytic, and magnetic properties of metal NPs plays pivotal role to manipulate and effect properties of metal NP-hydrogel composites. The synthesis of metal NP-hydrogel composites is accomplished by simple mixing of metal NPs, while in situ method involves use of

hydrogel (microreactor). The stability of metal NP-hydrogel composites is attributed to various chemical interactions between both components, i.e., (i) metal NPs and (ii) hydrogel with minimal chance of leakage [190]. In case of porous hydrogel, the reactants can diffuse through pores and reach metal NPs to react at their surface leading to desired product [172] (Figs. 1, 2, 3).

Silica particles have attracted much attention from researchers around the globe due to their unique characteristics, i.e., higher surface area, low density, and high stability (both chemical and thermal). Silica nanoparticles have been used as supporting material for metal NPs and also facilitate synthesis. For instance, eight times increase in the catalytic potential of Au NRs has been reported previously when immobilized on silica particle layers [192].

Organic materials have been extensively employed as stabilizing substance for immobilization of synthesized NPs [193]. The most commonly used supporting material is graphene that is 2D layer of carbon atoms arranged in regular array in the form of six-membered rings in-plane. Graphene has unique characteristics in terms of various electrical and mechanical properties along with thermal stability. Combining graphene with TiO₂ enhances its potential as supporting material for different nano assemblies. It is also reported that graphene alone has lower catalytic and stabilizing tendency as compared to its oxide form (GO), i.e., more superior in terms of reactivity than graphene. Similarly, reduced form of graphene oxide (rGO) has also been reported as efficient supporting material for immobilization of metal NPs [194] and suitable for potential applications in optoelectronics [195]. Nasrollahzadeh et al. reported combination of GO with TiO₂ as stabilizing medium for Ag NPs in the presence of *Euphorbia helioscopia* plant extract as reducing agent. This TiO₂-rGO with Ag NPs hybrid system showed significant catalytic potential for reduction of Congo red dye, and its structural illustration is as follows given in Fig. 4.

Organic-inorganic compounds

Organic-inorganic hybrid systems represent a novel dopant that has been utilized as supporting material to immobilize nanoparticles of interest for last few decades particularly for systems used in reduction of pollutants. Although this hybrid system is employed

Figure 1 **a** Magnetic NPs core-encapsulated polymer impregnated with metal nanoparticles, **b** metal nanoparticles-immobilized hydrogel network, **c** metal NPs impregnated fibrous nanosilica composite, **d** silica nanorattle encapsulated metal NPs core, **e** metal NPs immobilized on the surface of a hollow silica nanosphere; reproduced with permission from Naseem et al. [191].

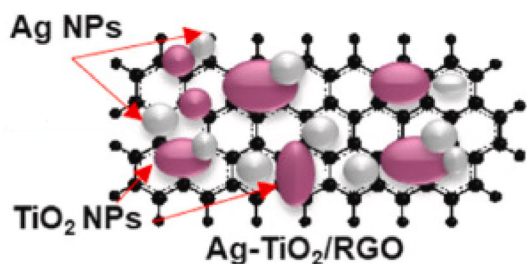
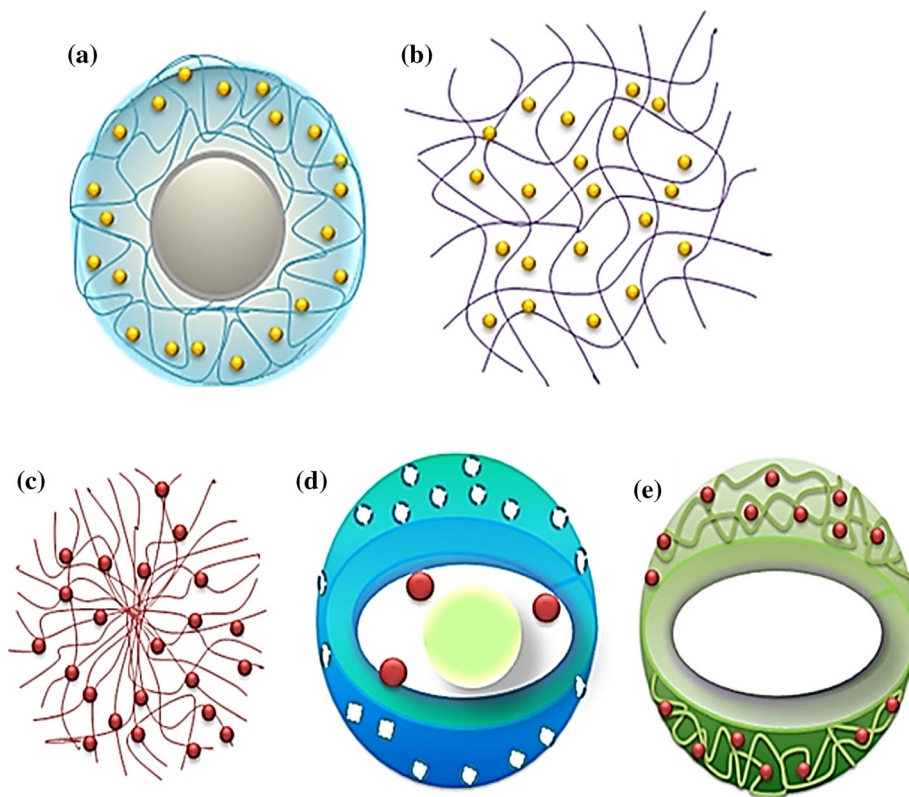


Figure 2 TiO_2/RGO with plasmonic silver nanoparticles; reproduced with permission from Bharath G. et al. [196].

with multiple applications still a lot of work is needed for optimization of various concerned parameters. Sravanthi et al. reported a hybrid biological system composed of bentonite clay (inorganic part) and Eucalyptus leaf extract (organic part) with significant catalytic potential for 4-NP reduction [197]. Similarly, gelatin represents another type of natural protein fibers as supporting material for metal NPs and is cost-effective as well. Different metal nanoparticle systems can be functionalized/impregnate on gelatin's surface and are uniformly distributed, while size of NPs is affected by pH and reaction time [198] Table 1.

Biogenic compounds

Various biological systems have been reported as stabilizing or support material like microorganisms, fungi, and extracts of different parts (i.e., stem, bark, and peel of fruit) for nanoparticle synthesis at large scale. The widespread use of these supporting materials in various systems is attributed to their availability, lower cost, non-toxic nature, eco-friendly, simple methodology, relatively cheap raw material, etc. These biological systems gained exceptional importance due to easier and mild reaction conditions involved in their synthesis. For instance, Dauthal and Mukhopadhyay [199] used fruit extracts of *Prunus domestica* (plum) as support medium for synthesis of Au NPs that also served as reductant where water-soluble polyols and amino acids are responsible for Au NPs reduction. Similarly, *B. rhamnoides* extracts serve as reducing agent for synthesis of AgNPs (accomplished reduction of Ag NPs in 2 h).

In conclusion, the application of various stabilizers have become a great necessity in the fabrication of efficient catalytic system and significant developments have been made in the recent years. Different

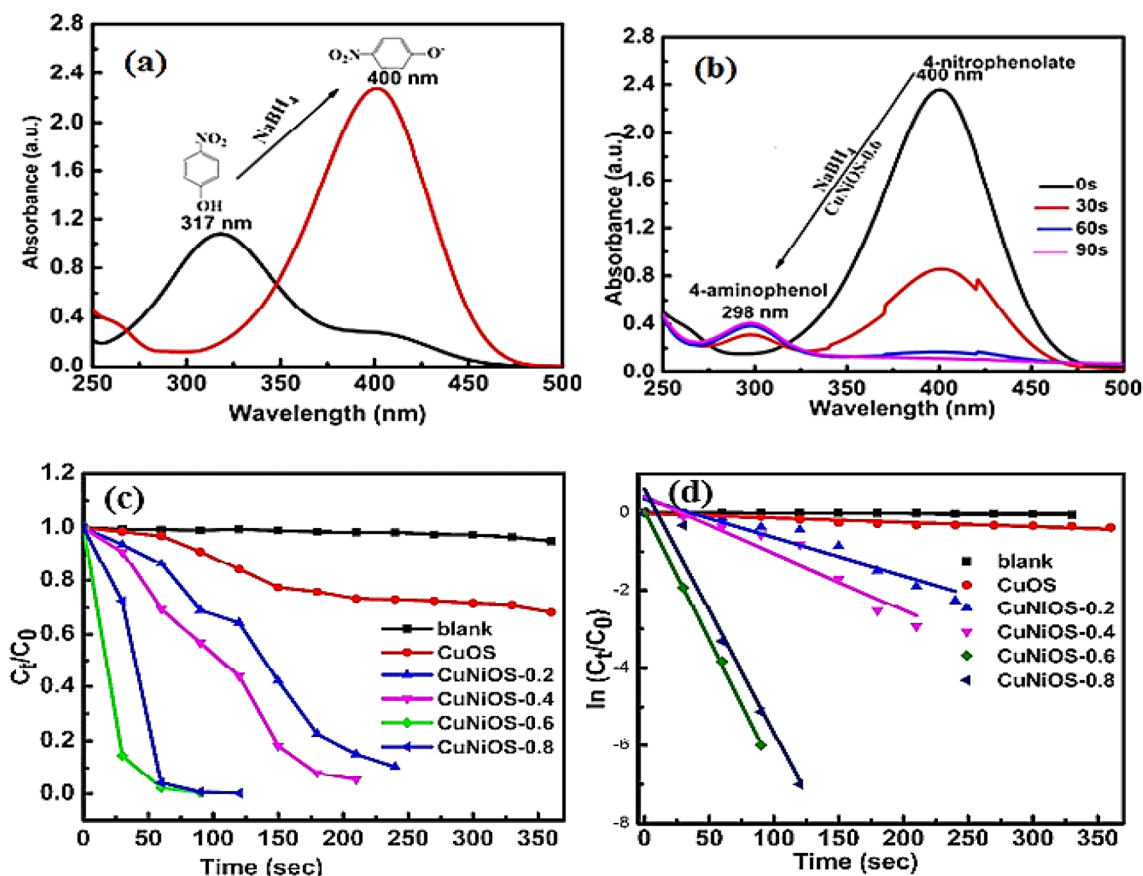


Figure 3 a UV–Vis spectra of 4-NP before and after the addition of NaBH₄ solution and b the time- dependent UV–vis absorption spectra for the reduction of 4-NP over CuNiOS-0.6 catalyst. Plots

of c C_t/C_0 , and d $\ln(C_t/C_0)$ versus reaction time (s) for reactions without catalyst and with CuOS and CuNiOS catalysts; reproduced with permission from Abay, A.K., et al. [207].

Figure 4 The possible reaction mechanism for the reduction of 4-nitro phenol (4-NP) by NaBH₄ over the CuNiOS-0.6 catalyst into 4-amino phenol (4-AP); reproduced with permission from Abay, A.K., et al. [208].

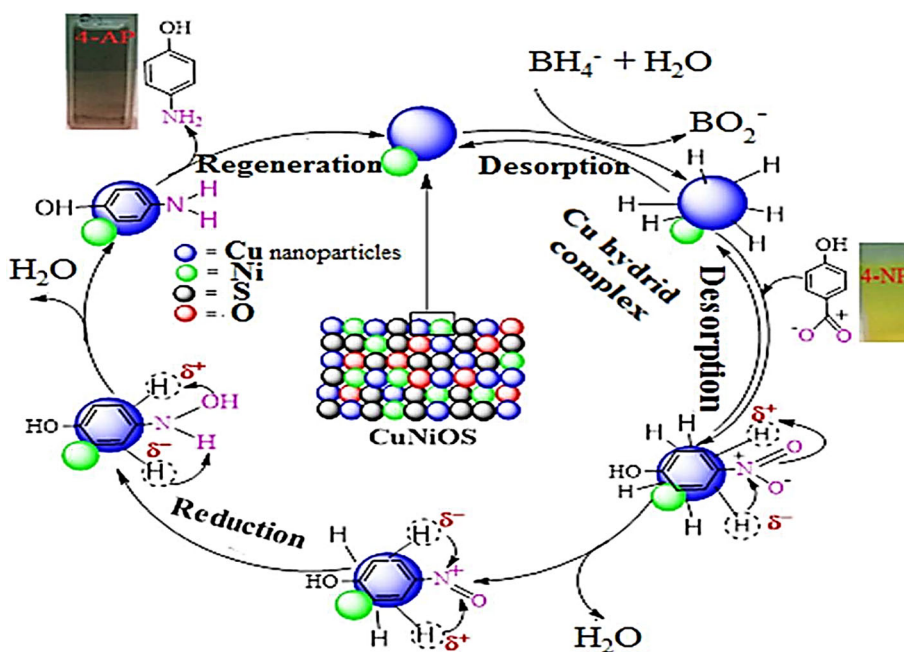


Table 1 Disadvantages of the main conventional techniques used for the wastewater treatment [68, 69]

Process	Limitations
Fentons reagent	Sludge formation with high iron contents, the deactivation of iron, and specific pH range (2.0–4.0)
Ozonation	Short half-life (20 min)
Photochemical	Formation of by-products
NaOCl	Release of aromatic amines
Cucurbituril	High cost
Electrochemical destruction	High cost of electricity
Activated carbon	Very expensive
Silica gel	Side reactions prevent commercial application
Membrane filtration	Concentrated sludge production
Ion exchange	Not effective for all dyes
Irradiation	Requires a lot of dissolved O ₂
Electrokinetic coagulation	High sludge production
Flotation froth flotation	High initial capital cost
Chemical precipitation	Chemical consumption, ineffective in removal of the metal ions at low concentration, physicochemical monitoring of the effluent (pH), high sludge production, disposal problems (management, treatment, cost)

kinds of stabilizing materials have been explored which have yielded outstanding results in the field. Polymeric compounds like dendrimers and hydrogels have been extensively utilized serving as capping agents to stabilize the metal NPs in the catalytic systems. In addition to that, organic–inorganic hybrid systems have also been introduced for this purpose, but still further improvements are required for the optimization of these hybrid systems. Several biogenic stabilizers have also been investigated owing to their eco-friendly nature, low cost, abundant availability, and simple fabrication.

Environmental concerns of nano catalyzed reduction of dye

Various types of catalysts have been reported for degradation of dyes by NaBH₄. Mostly, metal NPs have been employed for the reduction of environmental pollutants, but metal NPs themselves have toxic and adverse impacts on aquatic systems [200]. Secondly, NaBH₄ itself is a great threat for ecosystem as it is highly toxic and may harm lungs and nervous system. Therefore, an eco-friendly reducing agent (glucose and molecular hydrogen) should be used instead of NaBH₄ [201, 202]. Thirdly, it is reported that researchers are reducing toxic dyes into harmless

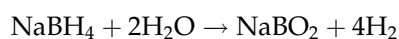
products, but toxic side products are still produced during the degradation reaction that is disturbing the natural environment [203]. Therefore, it is essential to recover nanocatalysts from the reaction mixture and fabricate nanocomposites that are financially feasible, clean, and eco-friendly. In addition, simple capping agents should be used to design efficient catalyst instead of using complex supporting materials that needed a lot of expertise and expensive chemicals. Green synthesized nanocatalysts are widely used for the reduction of organic pollutants being more economic, efficient, and easily recoverable. There is dire need to design environmentally benign and efficient nanocatalyst such as green nanocatalyst, as they are widely used for the reduction of organic pollutants and might be a good alternate to toxic reducing agents. Details over catalytic reduction of various dyes are provided as follows:

Catalytic reduction of nitrophenols

Nitrophenol is a highly poisonous environmental pollutant with carcinogenic and mutagenic effects on humans. To develop natural environment free from nitrophenols, it is necessary to reduce it into less toxic products that have applications in medicines, dye synthesis, photographic film developing methods, etc. Several catalysts like metal nanoparticles (MNPs),

impregnated silica, cefditoren, gelatin, graphene, porous glass filter plates, polymer, dextran, hydrogel, and bimetallic nanoparticles have been employed for the reduction of nitrophenols.

A general mechanism for the catalytic reduction of nitrophenols involves the Langmuir–Hinshelwood (L–H) adsorption model. At start of reaction, reactants (dye and NaBH_4) get adsorbed on the surface of NPs but NaBH_4 dissociates into its ions, and BH_4^- behaves as electron denoting species that transfer an electron to nitrophenol; later converted into aminophenol molecule. NaBH_4 releases hydrogen gas in the reaction mixture that not only increases rate of reaction but also decreases the induction time to activate the NPs by reconstructing its surface. Any impurity on nanocatalyst is removed by this H-flux, and more active site on the surface of NPs is available for the reaction [204–206]. The chemical reaction for release of H_2 gas can be written as follows:



In May, 2017, Abay et. al. fabricated a noble metal-free nanocatalyst with the structure CuNiOS , via eco-friendly and cost-effective approach, for effective degradation of organic dyes. The boosted catalytic performance of the bimetallic oxysulfide nanocatalysts was attributed to the synergistic effect between Ni and Cu atoms. The catalytic evaluation plots and a proposed degradation mechanism are given in Figs. 3 and 4, respectively.

Figure 3 depicts adsorption of BH_4^- ion, and transfer of hydride to CuNiOS -0.6-NP leading to the formation of Cu–H on the surface of catalyst. Simultaneously, the nitro group of dye captures H and electrons from Cu–H complex. Eventually, 4-AP is formed by hydrodeoxygenation reactions. The Ni in the catalyst enhances the activity of CuNiOS -0.6 by increasing electron flow, narrow the band gaps of the CuNiOS -0.6 and strong synergetic effect between nickel and copper atoms is one of the possible reasons to improve the catalytic activity of CuNiOS -0.6 as a nanocatalyst [208].

Various catalysts used for the degradation of 4-nitrophenol along with NaBH_4 (reducing agent) and degradation time are given in Table 2.

In another study, Chandra et. al. reported for the first time, the biosynthesis of Ag NPs functionalized with amino acid, using Neem gum for catalytic degradation of organic dyes. They utilized different

amino acid functional groups like alanine (Ala), tryptophan (Trp), histidine (His), glutamic acid (Glu), asparagine (Asp), and methionine (met) that exhibit strong affinity toward Ag^+ ions. Significant degradation of 4-NP was observed for the prepared samples as shown in Fig. 5. The enhanced catalytic activity was ascribed to the thermodynamic favorability offered by the suitable redox potential of Ag atoms lying in between the 4-NP and BH_4^- ions, hence acting as an electron relay.

Figure 5 represents the catalytic activity of AgNPs for reduction of 4-NP by NaBH_4 where addition of NaBH_4 into aqueous solution shifted peak to 400 nm due to formation of phenolate ion, while in the absence of AgNPs, very limited reduction of 4-NP to 4-Aminophenol by NaBH_4 was observed. Both AgNP and Trp-AgNP reduced 4-NP.

Catalytic reduction of methylene blue

The thiazine group forms the basic skeleton of methylene blue dye with λ_{max} 665 nm in an aqueous medium (due to $n-\pi^*$ transition) [235, 236]. In the absence of NPs, the reduction rate of methylene blue is very slow. Chandra et. al. demonstrated that Ag NPs bleach the methylene blue to colorless solution and their absorption peak (665 nm) is diminished, indicating the conversion of MB to Leuco MB (LMB). This confirmed the catalytic potential of the Ag nanoparticles against MB in aqueous and dodecyltrimethylammonium bromide (DTAB), sodium dodecyl sulfate (SDS), and dioctyl sulfosuccinate sodium salt (AOT) micellar mediums. Negative surface charge on silver NP resulted in significant adsorption of MB (cationic dye), by bringing them close to each other. Hence, strong non-covalent interactions among aromatic rings of the methylene blue ($\pi-\pi$ stacking) resulted in increased molecular association [235, 237, 238].

Micellar medium T-20 shows the reverse oxidation of leucomethylene blue in the presence of silver as nanocatalyst and absorbance spectrum (665 nm) increased linearly with time. This observation demonstrated that silver NPs played a vital role in the reverse oxidation of LMB to MB and presented a straight line through positive slope. Thus, rate of reverse oxidation is independent of NPs concentration, whereas it depends on the nature of the silver NPs. The clock reaction revealed significant use of the silver NPs as sensors for oxygen seepage in vacuum

Table 2 Some significant catalysts reported for the degradation of nitrophenols

Catalyst	Synthetic method	Degradation time	Reduction (%)	Ref
ZV-MNPs	Chemical approach (empty fruit bunch biomass residue)	10.0 min	97	[209]
C@Ni	Solvothermal	60 s	99.9	[210]
C@Cu	Solvothermal	60 s	99.3	[210]
AuNPs	Green synthetic approach using microwave	6 min	N/A	[211]
Pd/walnut shell	Green synthetic approach	1 min	99	[212]
Ag/CA beads	Phytogenic synthesis	0.5054 min ⁻¹	99	[213]
Pd/eggshell	Green and in situ reduction method	200 s	98	[214]
Ag NCs in PSS	Wet chemical	56 min	100	[215]
Ag NPs in PSS	Microwave heating	40 min	100	[215]
GO/Fe ₃ O ₄ /Pd	N/A	180 s	99	[216]
Ag NPs/Thymbra	Green synthesis	60 s	99	[217]
Resin-AuNPs	N/A	10 min	80	[218]
Ni-PVAm/SBA-15	N/A	20 min	98	[219]
Nap-Mg-Au	N/A	7 min	99	[220]
Au/CA	Green photochemical	45 min	97	[221]
Pd-FG	In situ co-reduction strategy	12 min	99	[222]
Au@PZS@CNTs	In situ reduction route	16 min	99.9	[223]
Au-GO	Electrochemical	30 min	99	[224]
Ag/KCC-1	Microwave-assisted hydrothermal	510 s	98	[225]
MCF-n-Ag-m	Plasma-assisted synthesis	5 min	98	[226]
p(AMPS)-Co	N/A	28 min	97	[227]
Polymer-anchored Pd(II)	Physicochemical route	5.5 h	99	[228]
Au/graphene	Hydrothermal	720 s	99.9	[229]
Fe ₃ O ₄ @C@Pt	Solvothermal method	60 min	N/A	[230]
KCC-1/Au	N/A	12 min	99	[231]
Cu@SBA-15	Hydrothermal	4 min	99.8	[232]
Ag/KCC-1	Microwave-assisted hydrothermal	510 s	98	[233]

packed food and for generating O₂ deficient environment in micellar and acidic aqueous mediums, where poisoning of catalyst occurs by oxygen [238] as depicted in Fig. 6.

In 2016, Saad et. al. fabricated a hybrid Ag-silica composite for the effective degradation of MB into LMB by binding aminopropyltriazole and 2-aminothiazole ligands to trap Ag particles effectively. They overcame the issue of aggregation and high surface energies of Ag NPs by using functional groups, hence improving their stability and efficiency. The reduction of MB to LMB followed the following mechanism; the cationic dye molecules accept electrons and H atoms from BH₄⁻ which result in π conjugation breaking the double bond between N and the aromatic rings of dye. The doubly bonded N atom in the dye molecule attaches a H atom by breaking the double bond, while the positively charged N atom receives an electron which result in π

conjugation of the dye molecule. The Ag NPs act as an electron relay between the two reactant species since their redox potential lies in between the MB and BH₄⁻ molecules. In the absence of Ag NPs, the reduction process was found to be extremely slow and limited [239]. The schematic structure of prepared Ag-silica composite and proposed mechanism for MB reduction are given in Fig. 7.

Various catalysts used for the degradation of methylene blue along with NaBH₄ (reducing agent) and reaction completion time are given in Table 3.

Catalytic reduction of Congo red

Congo red (CR) has linear symmetry with two phenyl rings in the center joined to two terminal naphthalene by diazo bonds [264]. The UV-Vis spectrum confirms (350 and 498 nm) the presence of azo linkages (-N=N-) in its basic structure [254]. It is a high toxic anionic dye that is widely used in paper, rubber, and

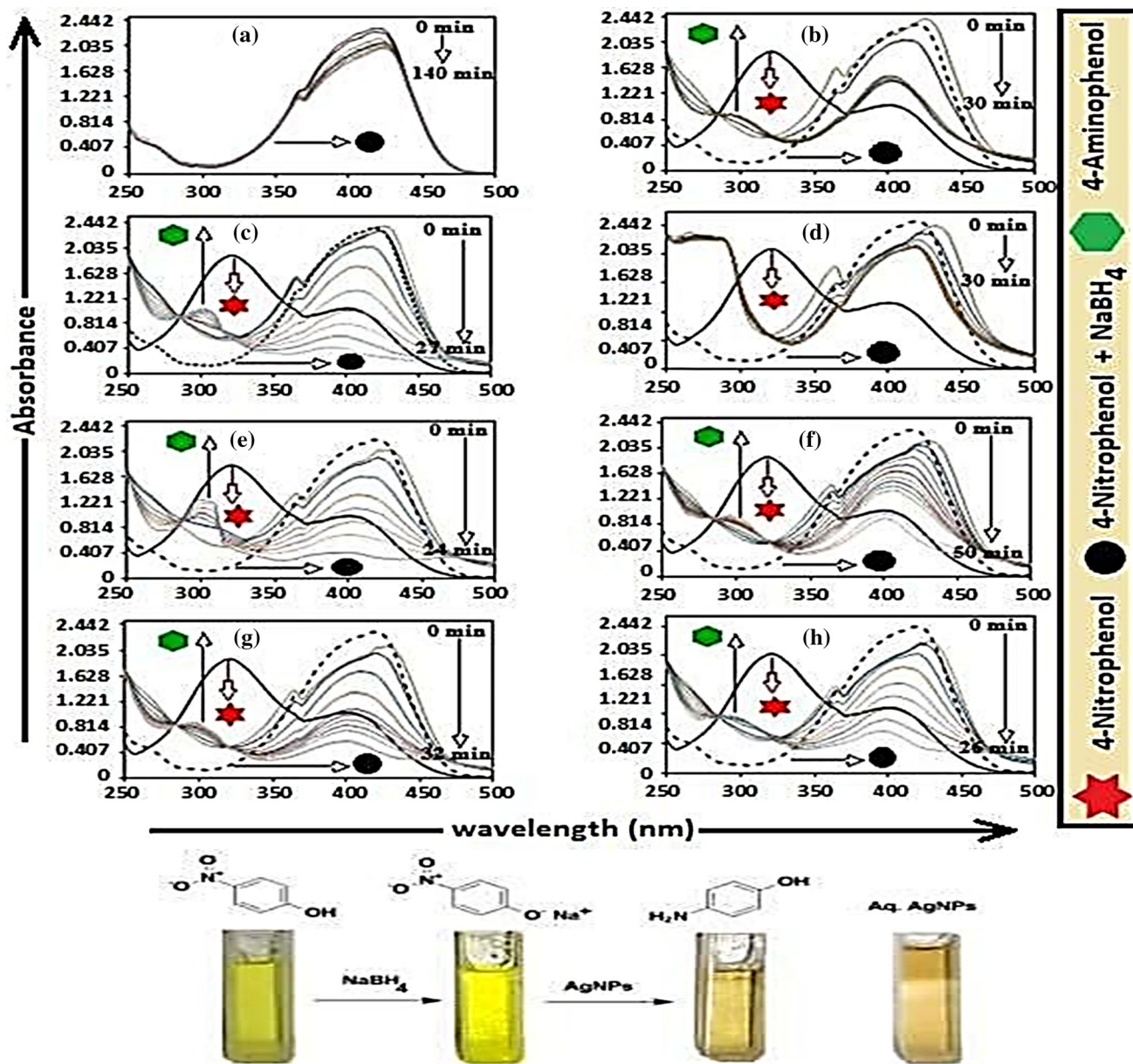


Figure 5 a Time-dependent UV–Visible spectra for the catalytic reduction of 4-nitrophenol by NaBH_4 a in the absence of AgNPs and in the presence of $30 \mu\text{M}$ AgNPs: b AgNP, c Ala-AgNP,

d Trp-AgNP, e Met-AgNP, f His-AgNP, g Glu-AgNP, and h Asp-AgNP; reproduced with permission from Chandra et al. [234].

textile factories and its degradation is needed to avoid its hazards [201] where azo bonds are degraded [70]. Only NaBH_4 is not enough for the reduction of CR molecule in an aqueous medium as this process is thermodynamically feasible but not kinetically. Actually, metal NPs provide large surface area for interaction of dye molecules and reducing agents that lead to final product. These nanocatalysts are not only involved in efficient reduction of dye molecules

but also make the reaction kinetically feasible (Figs. 8, 9, 10).

The catalytic potential of CR depends on different factors such as amount of reducing agent, concentration of catalyst, concentration of dye, a quantity of surfactant, and electrolyte [202, 204, 265–267]. A high dosage of catalyst provides large number of active sites for adsorption, increases the rate constant, and decreases the degradation time [203]. Nature of electrolyte also affects the catalytic potential during

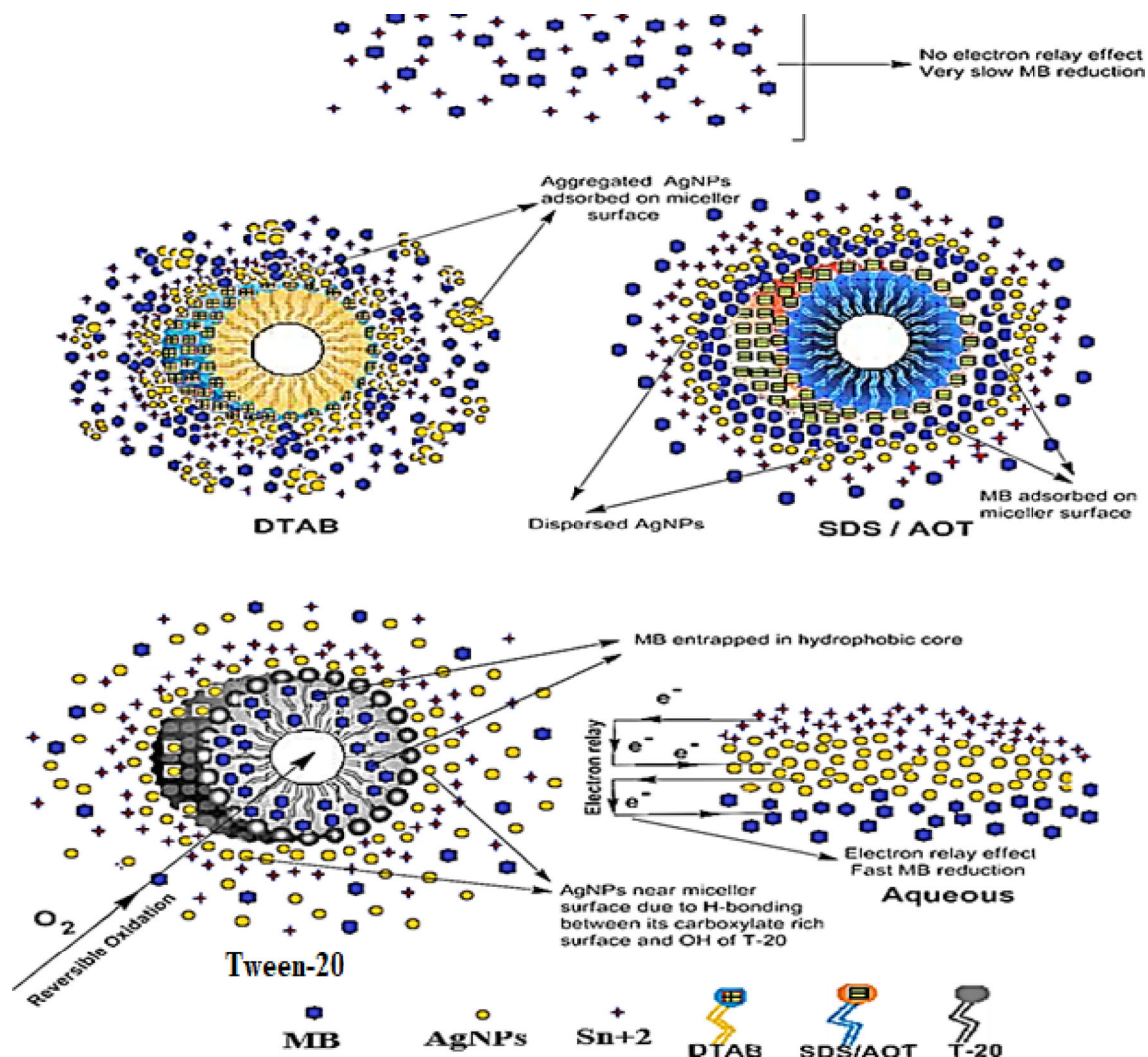


Figure 6 Schematic arrangement of MB, Sn^{2+} ions, and Ag NPs during catalytic reduction of MB by SnCl_2 as a reductant in aqueous and aqueous micellar mediums of SDS, AOT, DTAB, and T-20; reproduced with permission from Chandra et al. [234].

degradation. It influences the reduction rate in two ways; firstly, electrolytes increase the rate of reduction by transfer of charge from BH_4^- to Congo red via catalyst, and secondly, it decreases rate of reduction as it gets adsorbed on catalysts and block their active sites. Similarly, the catalytic potential of catalyst used for reduction of Congo red is also affected by surfactants due to their large amount in industrial drainage. Generally, they are adsorbed on the surface of MNPs and block their active sites. Some MNPs have negative charges; thus, large number of surfactants with positive charges can adsorb on the surface of catalyst and decrease the reduction rate of CR.

In 2013, Jia et. al. reported the use of palladium (Pd) NPs decorated on porous polypropylene hollow

membranes for the catalytic reduction of CR dye. They briefly studied the effect of dye concentration, Pd NPs, and reusability of membranes for catalytic activities. During catalysis, the Pd NPs with large amount of active sites act as electron relay, coordinate with π electrons of CR and surplus hydrogen atoms get adsorbed on catalyst surface. Further interaction of dye molecules with adsorbed surface results in the hydrogenolysis of the dye molecules. BH_4^- ions release hydrogen by donating an electron to MNPs and then attack CR molecules. Azo groups in Congo red are activated by electron carrying metal nanoparticles. In fact, CR molecules interact with MNPs through their sulfur and oxygen atoms and their azo double bonds are weakened via conjugation that ultimately breaks azo bond. Complete reduction

Figure 7 Schematic structure of AMT-SBA-15 and Tr-SBA-15 hybrid supports and mechanism of the catalyzed reduction reaction of MB to LMB in the presence of reducing agent; reproduced with permission from Saad A. et al. [239].

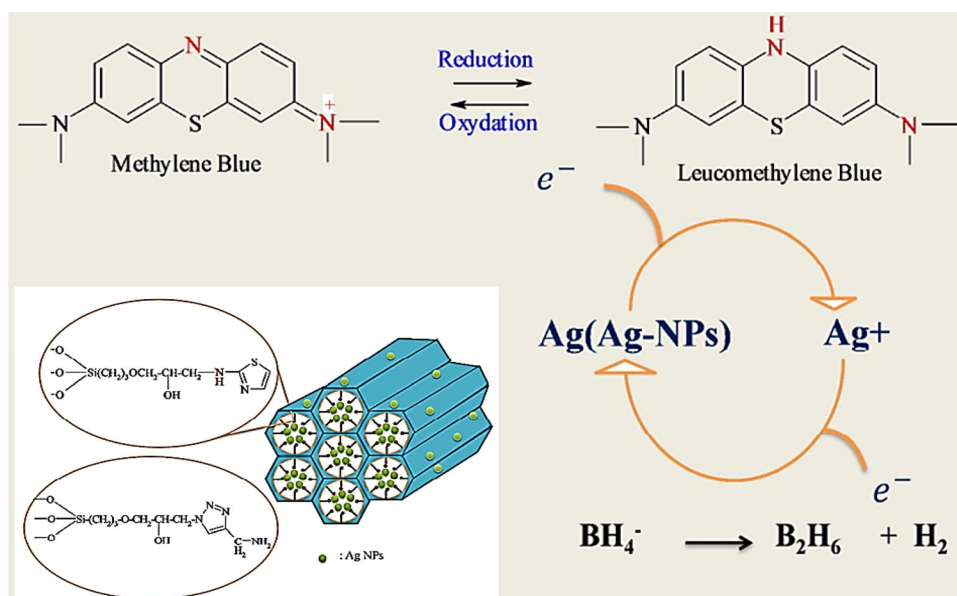


Table 3 Some significant catalysts reported for the degradation of methylene blue

Catalyst	Synthetic method	Degradation time	Reduction (%)	Refs
ZV-MNPs	N/A	5 min	99	[209]
Ag NPs/Peumo extract	Biosynthesis	< 1 min	99	[240]
C @Ni	Annealing method	60 s	98	[210]
CuO-NSs ^d	N/A	9 min	91	[241]
Ag/Cu/Au trimetallic NPS	Modified chemical synthesis	5–7 min	95	[242]
AS fruit peel extract AuNPs	Microwave-assisted rapid green approach	180 s	99	[243]
Pd/walnut shell	Green synthesis	13 s	99	[244]
Cu-CC-550	One-step heat treatment	270 s	99.8	[245]
Bentonite/Cu-NPs	Green synthesis	40 s	99.8	[246]
Ag NPs / clinoptilolite	Green synthesis	90 s	N/A	[247]
Cu/ZnO NPs	Green synthesis	Immediately	99.8	[248]
Ag/ZnO nanocomposite	Green synthesis	2 min	99	[249]
NiSe	Hydrothermal approach	3 min	99.9	[250]
Au/Fe ₃ O ₄ @C	Solvothermal route	10 min	99.9	[251]
Porous Cu microspheres	Wet-chemical reduction	8 min	98	[252]
SiNWAs-Cu	Ag-assisted chemical etching	10 min	N/A	[253]
Salmalia-AuNPs	Green synthesis	9 min	98.7	[254]
AgNPs/seashell	Green synthesis	2.5 min	99.8	[74]
Tragacanth/AgNPs	Green synthesis	12 min	99	[255]
Ag NPs on silica spheres	N/A	6.5 min	99	[256]
Au _{core} -PANI _{shell}	N/A	5 min	97	[257]
Fe ₃ O ₄ /Ag	Solvothermal synthesis	15 min	99.9	[258]
Ag/TiO ₂ nanocomposite	Green synthesis	70 s	99	[259]
PS/Ag	N/A	10 min	99	[260]
Au-PANI nanocomposite	One-pot interfacial synthesis	15 min	N/A	[261]
Fe ₃ O ₄ @PANI@Au	Surface polymerization	18 min	99.8	[262]
copper nanocrystals	Thermal reduction	130 s	99.8	[263]

Figure 8 **a** Reduction equation of Congo red; reproduced with permission from Rajesh et al., [268] and **b** proposed mechanism for the reduction of CR; reproduced with permission from. Jia et. al. [202].

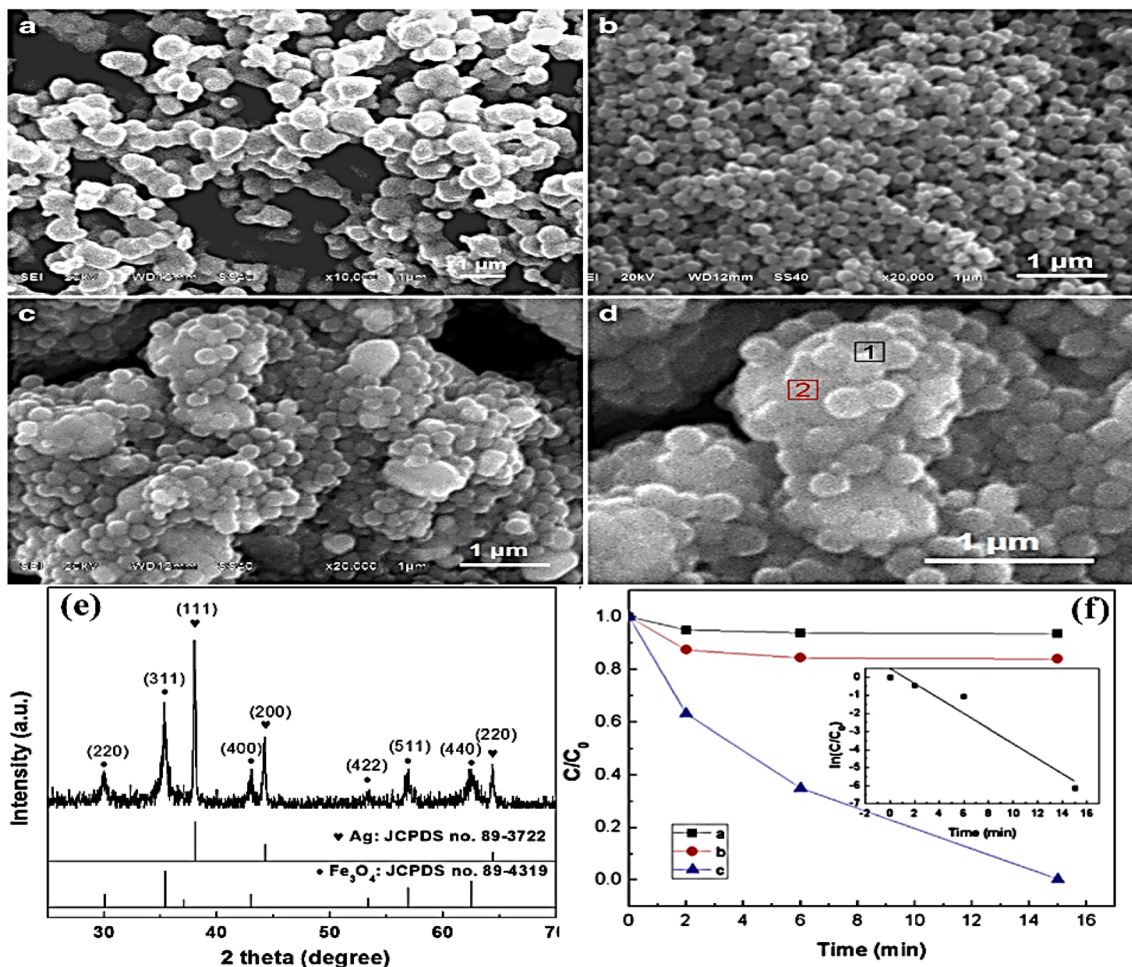
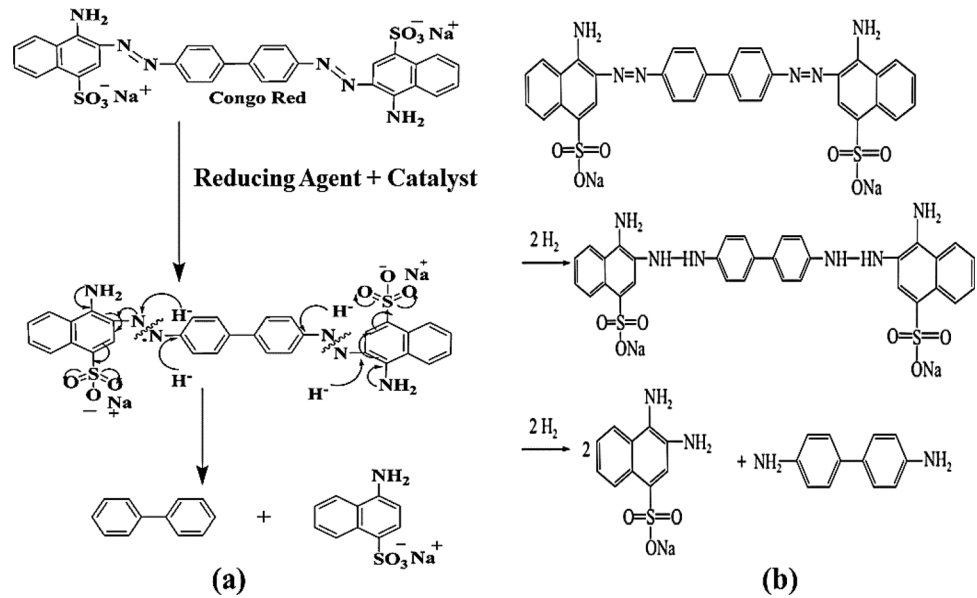


Figure 9 **a, b** SEM images of pure Ag, Fe₃O₄ and **c, d** the Ag-Fe₃O₄ composite, **e** XRD pattern of the Ag-Fe₃O₄ composite, **f** the reduction efficiency of RhB: **a** over Ag-Fe₃O₄ composite in the

absence of NaBH₄, **b** in the presence of NaBH₄ without Ag-Fe₃O₄ composite, and **c** over Ag-Fe₃O₄ composite in the presence of NaBH₄; reproduced with permission from Ai, L. et al. [258].

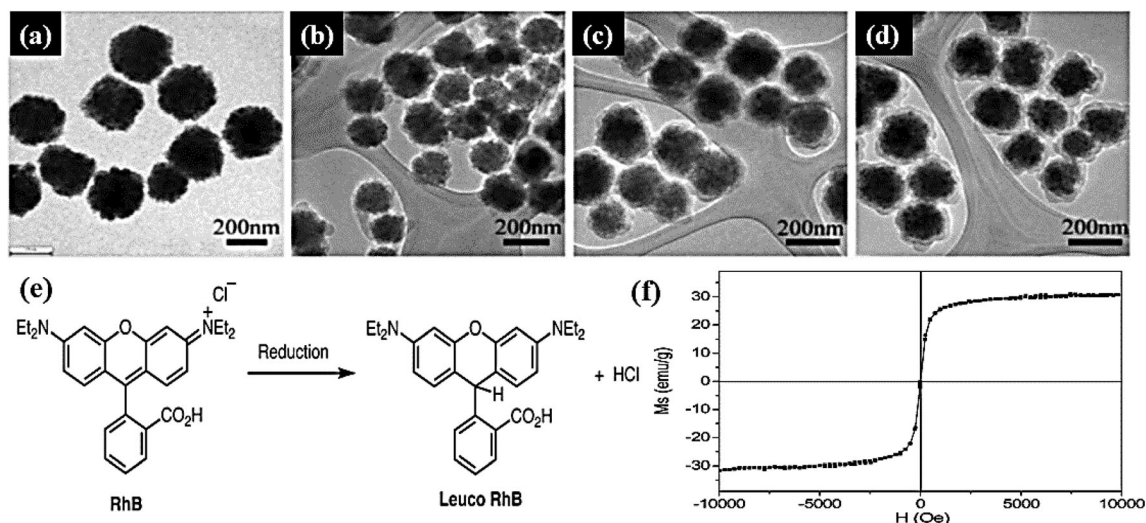


Figure 10 TEM images of the as-prepared Fe₃O₄@PANI core/shell nanocomposite with the PANI shell thickness of **a** 0 nm, **b** 7 nm, **c** 15 nm, and **d** 25 nm, **e** reduction of RhB into Leuco

of CR showed colorless solution due to conversion of $-N=N-$ into $-HN-NH-$ and later breaking of $-HN-NH-$ bond. The resulting products separated from surface of MNPs and diffused out into solution. MNPs store electrons after being transferred from BH_4^- ions during CR reduction [202].

Another study was reported by Rajesh et. al. in 2014, where they stabilized Au and Ag NPs on polyamidoamine (PAMAM) dendrimers functionalized graphene oxide (GO) for efficient catalytic degradation of azo dyes. The enhanced degradation of prepared nanostructures was attributed to larger surface area of GO and hydrophilic nature of PAMAM dendrimers molecules that helps in bringing the dye molecules closer to the active sites of the catalyst [203].

Catalytic reduction of Congo red by metal nanoparticles involves following steps as shown in Fig. 6 [203].

Catalytic reduction of RhB

RhB is another hazardous dye belonging to xanthene family, which is highly soluble in water, gives red color, and shows absorption maximum at 553 nm. Textile and food industries frequently utilize RhB dye as a colorant, and it has been frequently used for water tracing as well. However, RhB is extremely carcinogenic, neurotoxic and causes eye, respiratory tract, and skin irritation [269] Many studies have

RhB and **f** M-H curve of the Fe₃O₄@PANI@Au composite at room temperature; reproduced with permission from Xuan S., et al. [262].

been reported on the catalytic degradation of this hazardous dyes in the past few years.

Ai et. al. adopted the solvothermal route to fabricate Ag-Fe₃O₄ for catalytic reduction of Rhb dye in 2011. Furthermore, they gave the advantage of magnetically recycling the nanocatalysts and no significant decrease in catalytic activity was observed after three cycles. A significant increase of 16.8 times magnitude in catalytic rate for the reduction of RhB was reported in the presence of Ag-Fe₃O₄ in contrast to NaBH₄ used alone [257].

Xuan et. al. fabricated a magnetically responsive core-shell Fe₃O₄@polyaniline@Au nanocomposite via in situ surface polymerization (sound-assisted) method, in 2009. The superparamagnetic Fe₃O₄ proved to be easily recoverable magnetically, at room temperature. The nanocatalyst showed exceptional degradation of RhB dye where Au NPs acted as electron relay, receiving electrons from the nucleophile reducing agent to the electrophile dye molecules. This results in conversion of RhB to Leuco RhB as demonstrated in Fig. 10 [261].

Various catalysts used for the degradation of Rhodamine B along with NaBH₄ (reducing agent) and reaction completion time are given in Table 4.

Catalytic reduction of methyl orange

Du et. al. in 2017 fabricated Fe₃O₄ NPs coated with polydopamine (Fe₃O₄@PDA) for catalytic removal of

MO dye from wastewater. The prepared nanocomposite acted as a redox mediator due to the synergistic effect of Fe_3O_4 and PDA during the catalytic reduction of MO dye. In the catalytic reduction, Fe_3O_4 @PDA-NPs act as redox mediators that initiate catalysis by relaying electrons from BH_4^- to methyl orange. There are two possible ways for catalytic degradation of methyl orange. Firstly, the quinone parts of Fe_3O_4 @PDA-NPs are degraded by NaBH_4 and act as electron donors. Secondly, the quinone parts of Fe_3O_4 @PDA-NPs are reduced by NaBH_4 and donate electrons for the reduction of Fe^{+3} to Fe^{+2} and synergetic effect between Fe^{+3} and the quinone significantly enhances the catalytic potential of nanomaterial as demonstrated in Fig. 11 [272].

Furthermore, the reusability and stability of the nanocatalysts were also evaluated by magnetically recovering the catalysts and repeating the procedure again and again. An increase in reaction time was observed upon each recycle and possible reason was given for justification. A number of morphological and structural characterizations of samples before and after use were compared which showed no significant changes. However, TGA and ICP-MS analysis depicted a decrease in PDA and Fe^{3+} content of used catalyst which lead to decreased catalytic activity.

Various catalysts used for the degradation of MO along with NaBH_4 (reducing agent) and reaction completion time are given in Table 5.

Various catalysts used for the catalytic degradation of dyes along with preparation method, amount of catalyst, reaction completion time, and value of k_{app} are given in Table 6.

Recyclability of nanocatalysts

In heterogeneous catalysis, stability and reusability of nanocatalyst are very important from a financial point of view [298]. Mostly, nanocomposites are recycled from the reaction mixture and reused with significant efficiency even after 5 cycles (Atarod et al. 2016). However, a slight decrease in catalytic efficiency of NPs was observed after 5 cycles of usage. Gosh and co-workers have reported the recyclability of Cu-NPs loaded mesoporous silica SBA-15 and found that degradation reduction of dye was the same up to fifth cycle (Table 7).

Nasrollahzadeh et al. studied immobilization of Ag NPs on the surface of rGO-TiO₂ and reported a significant increase in recyclability of Ag-RGO-TiO₂ nanocomposite catalyst used for Congo red reduction [298]. The catalytic activity and morphology of given nanocomposite material were conserved up to 5th cycle of reusability. FE-TEM analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis confirmed that morphology of catalyst did not change and leakage of Ag NPs was also very low up to fifth cycle. Later, Zheng et al. reported even better nanocomposite materials having acrylic acid and chitosan-based hydrogels for impregnation of Ag NPs employed for Congo red reduction in an aqueous medium. They observed that catalytic potential of a given hybrid nanocatalyst composite was maintained up to ten successive cycles [299]. Similarly, shape, morphology, and size of Ag NPs-perlite assembly were maintained up to 4th cycle of reusability (i.e., EDX and TEM analysis) reported by Rostami-Vartooni and co-workers [266]. The increase in recyclability of Au NPs loaded Fe_3O_4 -polyaniline

Table 4 Some significant catalysts reported for the degradation of Rhodamine B

Catalyst	Synthetic approach	Degradation time	Reduction (%)	Refs
SiNWAs-Cu	Ag-assisted chemical etching	14 min	99	[253]
Fe_3O_4 @PANI@Au	An ultrasound-assisted in situ surface polymerization	18 min	99.8	[262]
Au-PANI nanocomposite	One-pot interfacial synthesis	15 min	N/A	[270]
Fe_3O_4 /Ag	Solvothermal synthesis	15 min	99.9	[258]
Cu@SBA-15	Hydrothermal	5 min	99	[232]
Pd/walnut shell	Green synthesis	0.21 min	99	[244]
Cu-CC-550 ^h	One-step heat treatment	180 s	99.8	[245]
MgAl-LDH@Au	Hydrothermal method	470 s	N/A	[129]
Ag@Cu	Green synthesis	5 min	99	[271]
Ag NPs/clinoptilolite	Green synthesis	90 s	98	[247]

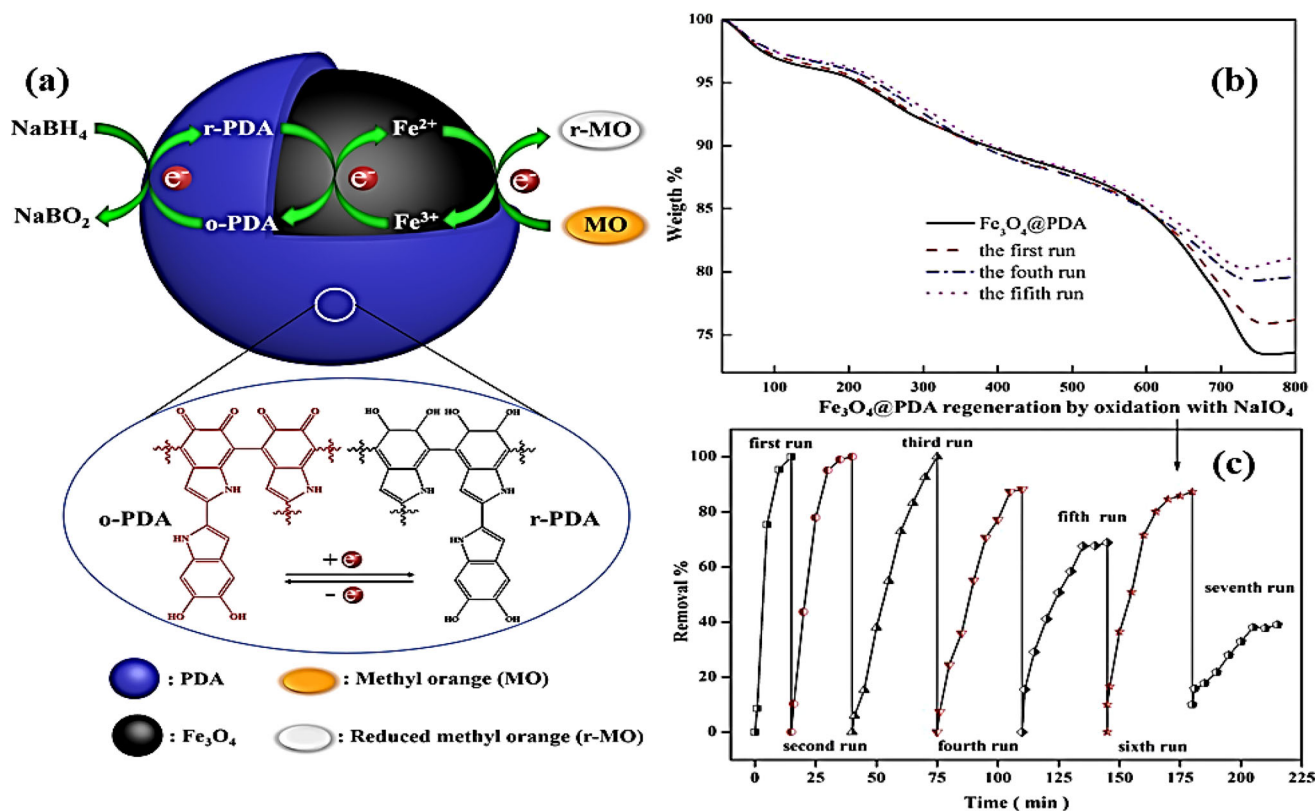


Figure 11 a Proposed mechanism for the reduction of dyes by NaBH_4 in the presence of Fe_3O_4 @PDA-NPs, **b** TGA curves of Fe_3O_4 @PDA-NPs for the fresh and deactivated catalysts, and

c decolorization rate of MO in the presence of Fe_3O_4 @PDA-NPs and NaBH_4 with catalyst recycling; reproduced with permission from Du S., et al. [272].

Table 5 Some significant catalysts reported for the degradation of methyl orange

Catalyst	Synthetic approach	Degradation time	Reduction (%)	Refs
Cu@SBA-15	Hydrothermal	5 min	99.8	[232]
Ag/ Fe_3O_4 nanocomposite	N/A	110 min	99	[273]
Ag/ TiO_2 nanocomposite	Green synthesis	9 min	99	[259]
ZV-MNPs	Chemical approach (empty fruit bunch biomass residue)	4 min	97	[209]
C @Ni	Solvothermal	60 s	98	[210]
C @Cu	Solvothermal	60 s	97	[210]
Cu/sodium borosilicate	Green synthesis	2 min	95	[274]
Pd/walnut shell	Green synthetic approach	Immediately	99	[244]
PdNPs	Green synthetic approach	5 min	98	[244]
MgAl-LDH@Au	Hydrothermal method	210 s	N/A	[129]
MgAlCe-LDH@Au	Hydrothermal method	90 s	N/A	[129]
Pd/eggshell	Green and in situ reduction method	2 min	98	[275]
Ag/ZnO	Green synthesis	4 min	97	[249]
Ag NPs /clinoptilolite	Green synthesis	138 s	99	[247]

composite material was studied by Chen et al. who reported the catalytic potential of this composite up to 5th cycle of reuse [300]. ICP-MS and TEM analysis

confirmed no change in size of nanoparticles while same tendency was observed in case of Au NPs immobilized on tubular Kappa fiber and activity was

Table 6 Some significant catalysts reported for the degradation of various organic dyes

Catalyst	Preparation	Dye	Catalyst (g)	k	k_{nor} ($s^{-1}g^{-1}$)	Refs
ZBD@Ag	TA/ZBD with Ag^+	MB	0.0002	$0.0061 s^{-1}$	30.5	[276]
Anionic AgNPs colloids	Ag^+ with oleic acid and n-butylamine	MB	0.02	$0.00003 s^{-1}$	0.001	[277]
Multihollow polymer/Ag	Ag^+ with as-prepared P(St-Nass)	MB	0.01	$0.002 s^{-1}$	0.2	[278]
Fe ₃ O ₄ @PDA-Ag-10	Ag^+ with Fe ₃ O ₄ @PDA core-shell	MB	0.01	$0.007 s^{-1}$	0.71	[279]
Fe ₃ O ₄ @COF-Au	Solvothermal method	4-NP	0.003	$3.7 \times 10^{-3} s^{-1}$	-	[280]
AFs-0.1	AgNO ₃ and natural cotton	4-NP		$0.4199 min^{-1}$	-	[281]
MC-PDA-Ag	Pyrolysis of Fe loaded pine sawdust	MB	0.01	$0.873 min^{-1}$	-	[282]
MOF-Derived MxSy@Composites	Sulfurization and calcination of MOF-	MB	0.04	$0.0003 s^{-1}$	0.0092	[283]
Fe-GAC	Fe ³⁺ ions with GAC(Granular Activated Carbon)	MB	0.2	$0.00038 s^{-1}$	0.0019	[284]
MHNTS-PDA-Au	Au ions with polydopamine functionalized MHNTs	MB	0.004	$0.08 s^{-1}$	20	[285]
P(TA)-Cu ILs	Reaction of P(TA) particle with CuCl ₂ solution	MB	0.027	$0.015 s^{-1}$	0.55	[286]
Cu/CuO-Ag	Ag ions with Cu/Cu- O suspension	MB	0.01	$0.0014 s^{-1}$	0.14	[287]
Fe ₃ O ₄ @PDA-Ag microsphere	Adding Fe ₃ O ₄ @PDA to silver ammonia solution	MB	0.005	$0.029 s^{-1}$	5.93	[288]
3D-graphene/Ag	Reaction of Ag ions with GO solution	MB	0.005	$0.0041 s^{-1}$	0.83	[289]
Au@TA-GH	Reaction of TA-GH with HAuCl ₄ solution	MB	0.002	$0.0051 s^{-1}$	2.5	[290]
CuNiOS-6	Facile solution-based technique	4-NP	-	$0.070 s^{-1}$	0.0070	[208]
		MB		$0.144 s^{-1}$	0.0144	
		RhB		$0.130 s^{-1}$	0.0130	
Cu + Co@OPF	Metal NPs decorated oil palm frond (OPF) via facile chemical route	CR	0.015	$7.8 \times 10^{-2} s^{-1}$	-	[291]
		MO		$3.2 \times 10^{-1} s^{-1}$		
		RB		$2.66 \times 10^{-1} s^{-1}$		
		MB		$1.775 \times 10^{-1} s^{-1}$		
		ONP		$2.99 \times 10^{-2} s^{-1}$		
		MNP		$3.96 \times 10^{-2} s^{-1}$		
		PNP		$1.29 \times 10^{-1} s^{-1}$		
		DNP		$2.43 \times 10^{-2} s^{-1}$		
Fe ₃ O ₄ @TA/Ag	Tannic acid and Fe ₃ O ₄ NPs via chemical coprecipitation method	MB	0.002	$0.0685 s^{-1}$	-	[292]
		4-NP		$0.0436 s^{-1}$		
		RhB		$0.0516 s^{-1}$		
C @Ni	Annealing of Ni-BDC and Cu-BDC	4-NP	0.001	$0.075 s^{-1}$	-	[210]
		MO		$0.123 s^{-1}$		
		MB		$0.114 s^{-1}$		
C @Cu	Annealing of Ni-BDC and Cu-BDC	4-NP	0.001	$0.059 s^{-1}$	-	[210]
		MO		$0.062 s^{-1}$		
		MB		$0.089 s^{-1}$		
Fe ₃ O ₄ /SiO ₂ -Pr-S-Ag	Thiol groups and Fe ₃ O ₄ nanoparticles	MB	0.002	$0.138 s^{-1}$	-	[293]
		4-NP		$0.0321 s^{-1}$		
		RhB		$0.0646 s^{-1}$		
Au NPs	Peptide (Ac-FFACD-OH) and Au ⁺	4-NP	-	$0.014 s^{-1}$	-	[13]
		MO		$0.019 s^{-1}$		
		MB		$0.21 s^{-1}$		
		RhB		$0.0015 s^{-1}$		
Ag NPs	Peptide (Ac-FFACD-OH) and Ag ⁺	4-NP	-	$0.0061 s^{-1}$	-	[13]
		MO		$0.015 s^{-1}$		
		MB		$0.00040 s^{-1}$		
		RhB		$0.0021 s^{-1}$		

Table 6 continued

Catalyst	Preparation	Dye	Catalyst (g)	k	k_{nor} ($s^{-1}g^{-1}$)	Refs
Ag NPs/fibers	Peptide (Ac-FFACD-OH) and Ag^+	4-NP	–	$0.014 s^{-1}$	–	[13]
		MO		$0.014 s^{-1}$		
		MB		$0.0019 s^{-1}$		
		RhB		$0.022 s^{-1}$		

Table 7 The comparison of kinetic (pseudo first and second order) of degradation of dyes by various reported photocatalyst to explore the degradation ability of nanocatalyst

Substrate	Dye	Pseudo-first order		Pseudo-second order		Refs
		K1	R1	K2	R2	
AMPS/AA	MB	$0.0442176 (min^{-1}) 10^{-2}$	0.95	$4.15 (g mg^{-1} min^{-1}) 10^{-5}$	0.99	[294]
AMPS/AA-Fe3O4	MB	$0.03224 (min^{-1}) 10^{-2}$	0.94	$5.7 (g mg^{-1} min^{-1}) 10^{-5}$	0.99	
AMPS/AA-Ag	MB	$0.0925806 (min^{-1}) 10^{-2}$	0.78	$6.95 (g mg^{-1} min^{-1}) 10^{-5}$	0.99	
Blank	MB	$14.7 (min^{-1}) 10^{-3}$	0.98	$2.4 (mg/L. min) 10^{-3}$	0.99	[295]
AgNPs	MB	$130 (min^{-1}) 10^{-3}$	0.99	$56.8 (mg/L. min) 10^{-3}$	0.83	
Ag-AuNPs	MB	$121 (min^{-1}) 10^{-3}$	0.99	$51.8 (mg/L. min) 10^{-3}$	0.88	
Ag-Au-PdNPs	MB	$1004 (min^{-1}) 10^{-3}$	0.94	$1159.2 (mg/L. min) 10^{-3}$	0.61	
Blank	MO	$15.1 (min^{-1}) 10^{-3}$	0.99	$2.7 (mg/L. min) 10^{-3}$	0.77	
AgNPs	MO	$56.3 (min^{-1}) 10^{-3}$	0.98	$16.4 (mg/L. min) 10^{-3}$	0.72	
Ag-AuNPs	MO	$42.1 (min^{-1}) 10^{-3}$	0.99	$7.8 (mg/L. min) 10^{-3}$	0.95	
Ag-Au-PdNPs	MO	$711.9 (min^{-1}) 10^{-3}$	0.93	$282.8 (mg/L. min) 10^{-3}$	0.67	
Fe3O4	MB	$3.6312091 (min - 1)$	0.907	$0.00617457 (mg - 1 \cdot min - 1)$	0.9643	[296]
AgNPs/GG/poly (AA) NP	MB	0.039	0.983	1.627×10^{-3}	0.999	[297]

maintained up to 10th cycle [301]. Furthermore, immobilizing Cu-NPs on surface of chitosan also showed increase recyclability for reduction of Congo red [302]. Plenty of research work has been reported for hybrid nanocomposites used for Congo red degradation [104, 301, 303]. Various other nanocomposites have been reported with natural heterogeneous catalysts that can be separated easily through mild centrifugation. Easy recovery and higher catalytic activity of these nanocomposites have attracted industries to make use of them and replace expensive catalyst for catalytic reduction of Congo red.

Recycling efficiency is the most significant aspect of a catalyst from economical point of view. Ansari et al. carried out recycling study of Co nanocatalysts entangled in p(AAc) networks using p(AAc)-Co composite as catalyst for the reduction of 4-NP up to four consecutive cycles. In this task, composite was removed out of the reaction medium after catalysis

via filtration, accompanied by washing with distilled water. Under the same set of conditions, composite was again applied as catalyst for the same reaction [304]. With every cycle, change in activity of catalyst was observed and is depicted in Fig. 12.

Azzam et al. determined the reusability of the $TiO_2@CNTs/AgNPs/C10$ nanocomposite by employing the same photocatalyst repeatedly for 5 cycles. Figure 13 signifies a decrease in photocatalytic activity of nanocomposite hardly from 100 to 92% within three cycles and then became 77% at the fifth cycle depend on the prescribed environments. Hence, obtained results showed that the synthesized nanocomposite is an efficient and stable photocatalyst within three cycles [305].

Das et al. studied the reusability of magnetic nanocatalyst $Fe_3O_4@PPy-MAA/Ag$ for reduction of 4-NP. After the reduction of 4-NP, catalyst was dissociated easily from the reaction mixture with a

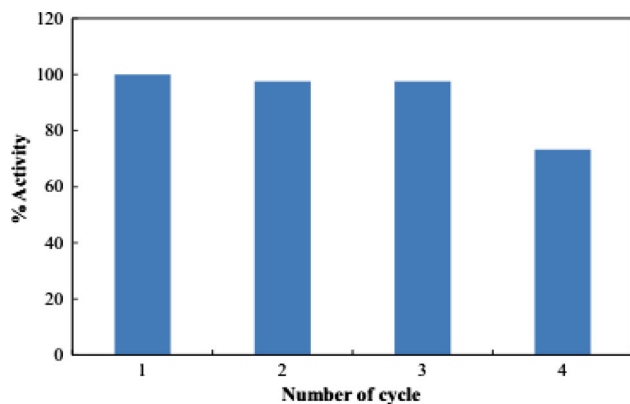


Figure 12 Effect of recycling on catalytic activity in terms % activity of p(AAc)-Co composite catalyst as a function of number of cycle. Reaction conditions; 0.001 M NP = 50 ml, NaBH_4 = 0.19 g, Catalyst = 0.03 g of Co, 250 rpm, 30 °C; reproduced with permission from Ansari et al. [304].

magnet due to its intrinsic magnetism and washed five times by distilled water before reusing in further recycling. Figure 14 reveals that the catalyst was effectively reused in eight successive cycles of 30 min reaction time each. Moreover, it was also monitored that Fe_3O_4 @PPy-MAA/Ag had not showed any remarkable loss of activity after seven cycles. Using nanocatalyst, more than 80% conversion of 4-NP to 4-AP was acquired after eight successive cycles which shows extraordinary stability. and robustness of nanocatalyst toward multiple cycles of reuse [306].

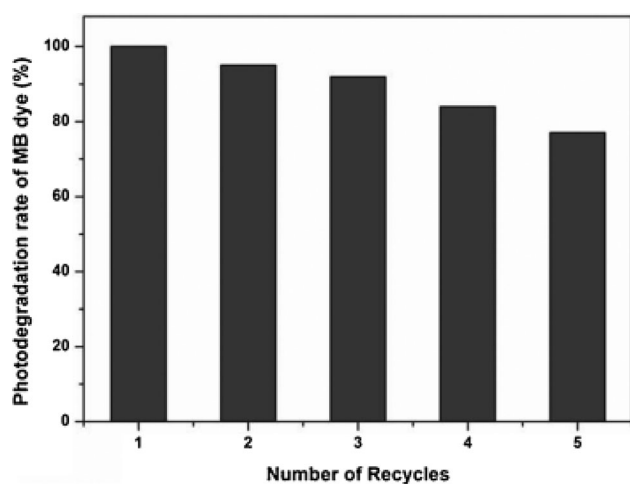


Figure 13 Recycles of TiO_2 @CNTs/AgNPs/C10 nanocomposite during photodegradation of MB dye [C_0 = 20 mg/L, catalyst dose = 0.5 g/L, H_2O_2 = 0.782 mol/L, pH = 5.8, contact time = 120 min, and $T = 25$ °C]; reproduced with permission from Azzam et al. [305].

Ding et al. studied the photocatalytic stability of Ag/Ag₂O/ZnO nanocomposite using visible light irradiation by cyclic degradation of MB for four times. Figure 15 signifies that the synthesized nanocomposite exhibits excellent photocatalytic stability. After 50 min, 99% degradation of MB was observed in the first run. In the second and third run, high degradation efficiency (99%) was monitored till the fourth run down to 85% [307].

Advanced spectroscopy techniques

In order to understand the interaction mechanism involved between the nanocatalysts and the pollutants to be degraded, several spectroscopic techniques have been adopted by the research community in the past. The interaction mechanisms are highly dependent on the nature of the pollutants/dyes (organic or inorganic, molecular structure, redox conditions, and coordination components), the morphological features of nanocatalysts (porous structure, positive/negative net charge on the surface, attached functional groups and stability), and the atmospheric conditions (pH, temperature, and ionic composition). Depending on these conditions, different kinds of interaction mechanisms including adsorption, precipitation, ion exchange, redox reactions, photocatalytic degradation, and surface complexation, etc., can be followed. Several advanced spectroscopic techniques like X-ray photoelectron

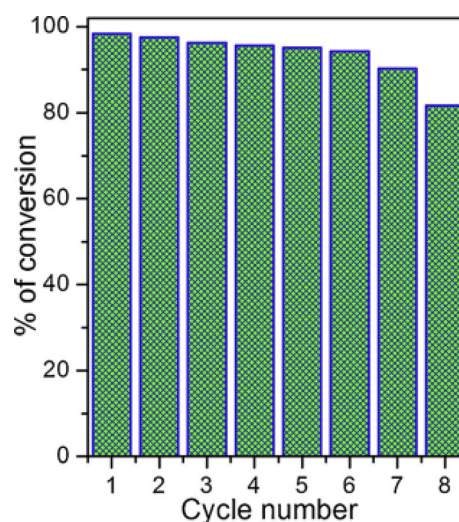


Figure 14 Reusability of Fe_3O_4 @PPy-MAA/Ag nanocatalyst over eight successive cycles for reduction of 4-NP; reproduced with permission from Das et al. [306].

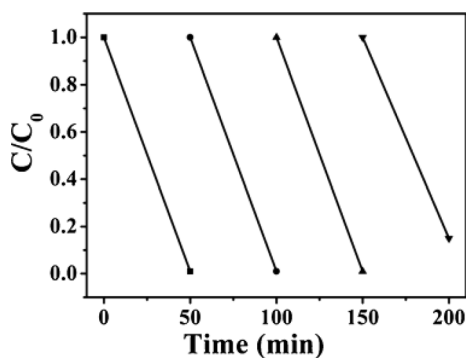


Figure 15 The cyclic stability of the Ag/Ag₂O/ZnO nanocomposite as a photocatalyst to degrade MB for four cycles under visible light irradiation; reproduced with permission from Ding et al. [307].

spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and X-ray absorption fine structure spectroscopy (XAFS) have been adopted to evaluate the interaction mechanisms. Some semi-qualitative information can be inferred by observing the shift in peaks position (red/blue shifts) or the intensity of the peaks generated in these spectroscopic techniques.

For instance, we can get some useful information regarding the chemical composition, oxidation state, binding energy, and relative content for the surface or near surface interactions through XPS [308, 309]. Recently, Markovic et al. employed XPS analysis to study the chemical composition of the prepared CoAP catalyst and confirmed the oxidation state of cobalt (Co⁺²) present in the samples [310]. The bond lengths between the metal atoms along with coordination number and valence state can be significantly evaluated by utilizing XAFS analysis. With this information provided by the XAFS, the microstructure can be evaluated molecularly and some interaction information can be inferred semi-qualitatively/quantitatively as well [311]. Mohamed et al. employed the extended EXAFS technique to evaluate the binding and particle size of Cu in TiO₂-SiO₂ catalyst for the catalytic degradation of Direct Blue dye [312]. In another study, Choi and colleagues evaluated the coordination number of Cu atoms in Cu/Cu₂O/CuO-rGO catalysts by applying EXAFS analysis and measured the bond lengths of metal atoms as well [313]. The presence of other relevant phases of Co in Co-B-O nanocatalysts was confirmed by Edla et al. through the EXAFS analysis and no other phases were detected [314]. The EXAFS spectra of prepared catalyst were compared with the pure

Co₃O₄ powder to infer this information as shown in Fig. 16.

FTIR analysis is extensively employed to evaluate the chemical composition and functional groups present in catalyst in order to understand the interaction mechanisms. For instance, Han et al. confirmed the desulfuration phenomenon by evaluating the diminishing FTIR peak of -SO₃Na during the degradation of methyl orange over Cu-MgAl catalysts [315]. In a recent study, Lai and colleagues evaluated the interaction between Ag NPs and dandelion extract molecules with the help of FTIR analysis. The analysis revealed the capping of AG NPs with dandelion extract which acted as a reducing agent in the degradation of MO and RhB dyes [316].

Computational analysis

For better quantitative analysis of the interaction mechanism at molecular level, computational approaches have gained increasing recognition as a power tool in the field of catalysis. This computational modeling allows us to deeply probe the mechanisms occurring at molecular level which cannot be evaluated experimentally. One can explore the dynamics, structure, energetic, and the interaction mechanisms even at atomic scale level by adopting these modeling techniques effectively. Generally, the

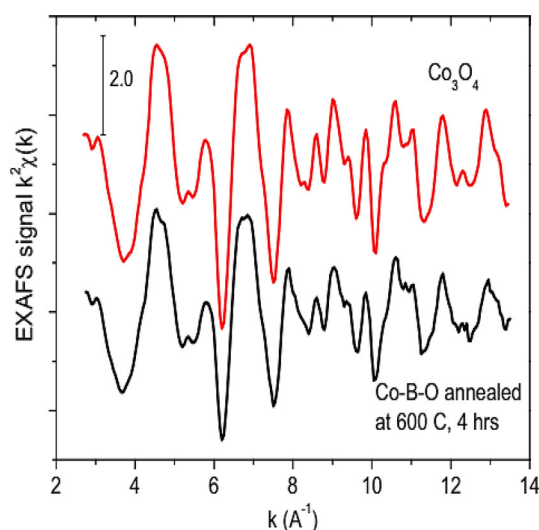


Figure 16 EXAFS spectrum of Co-B-O coating on glass after annealing in air for 4 h at 600 °C, compared to the very similar spectrum of Co₃O₄ crystalline powder; reproduced with permission from Elda R., et al. [314].

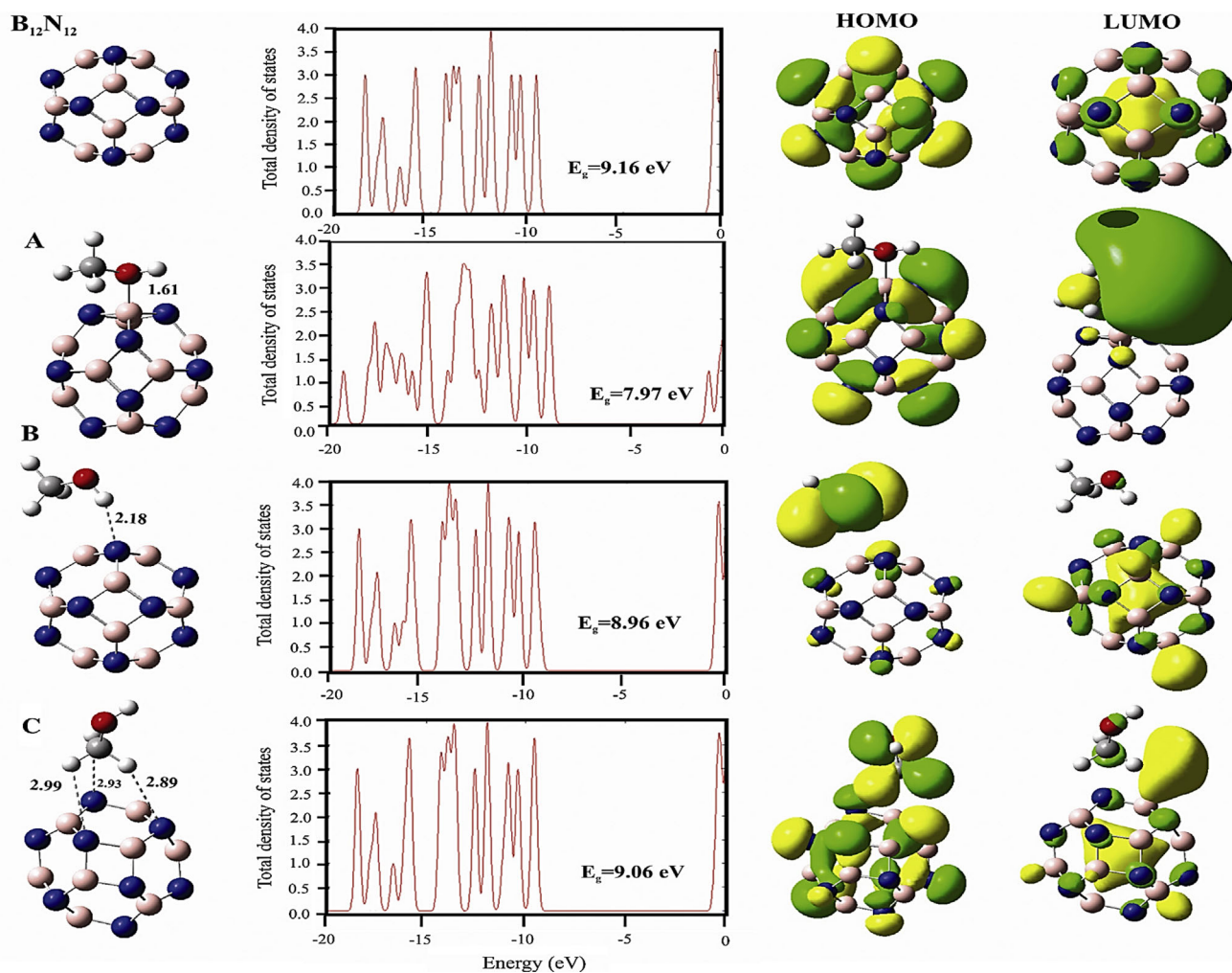


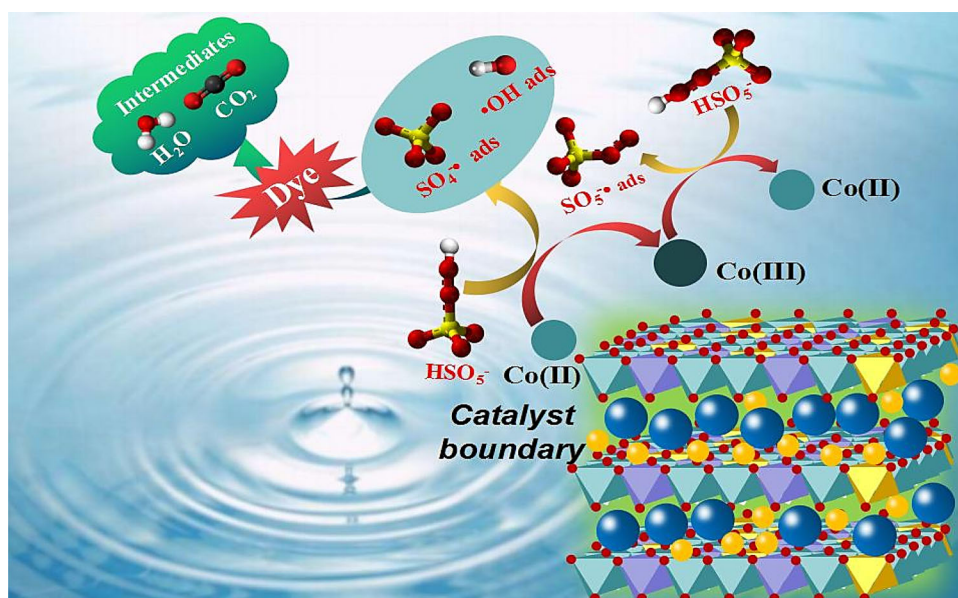
Figure 17 Optimized structures, total density of states, HOMO and LUMO of B₁₂N₁₂ and B₁₂N₁₂ACH₃OH complexes. Distances in Å.; reproduced with permission from Esrafil et al. [319].

catalytic systems involve the adsorption of reactant species on the surface of catalyst and undergo different types of interactions including ion exchange, electrostatic interactions, redox reactions, and complexation. The computational analysis can provide a compact information about which of the possible mechanisms are most probable to happen in a given system. Recently, Zhang et al. have demonstrated a density functional theory (DFT) analysis of the degradation mechanism involved in the oxidation of 1, 2-dichloropropane (DCP) over LaMnO₃ perovskite catalyst. The DFT modeling revealed that the chemisorption of 1, 2-DCP molecules on the active Mn sites results in the heterogeneous degradation of the organic pollutant into allyl chloride, while the further decomposition of allyl chloride is highly dependent on the reaction conditions [317]. Cherian

and colleagues designed a DFT model for the light driven catalytic activity of Co, N, and Co–N-doped MoS₂ films and concluded that N-doped films were best candidates for the photocatalytic degradation of dyes. Moreover, the study revealed that stability of MoS₂ decreased along with increase in band gap values upon doping [318]. The adsorption energies, equilibrium geometries, and dissociative reactions involved in the degradation of methanol over full-ene like B₁₂N₁₂ catalyst have also been evaluated via DFT modeling [319]. The adsorption of methanol on the B₁₂N₁₂ catalyst also tends to enhance the electric conductivity of the material and O–H bond breaking was proposed as the most probable way of methanol decomposition (Figs. 17, 18).

Matos and colleagues used DFT modeling to study the photocatalytic degradation mechanism of

Figure 18 Dye degradation mechanism along with computational model of ternary CoFeNi-layered double hydroxide catalyst; reproduced with permission from Zeng et al.[322].



methylene blue and phenols over C-doped TiO₂ catalyst. They concluded that the total electronic charge on oxygen atoms bonded with TiO₂ increased after incorporation of carbon in the lattice [320].

Apart from DFT, frontier molecular orbital theory (FMT) has also been adopted by the researchers to understand the interaction mechanisms involved in catalytic degradation of organic pollutants. For instance, Zanjanchi and colleagues studied the adsorption kinetics and reaction of 1-aryazo-2-naphthol dyes with the surface of cellulose. The computational analysis revealed that the singlet-state oxygen (¹O₂) acts as electrophile and takes part in electrophilic reaction to oxidize the dye molecules [321]. Recently, Zheng et al. studied the interactions of Congo red and RhB dyes with ternary CoFeNi-layered double hydroxide catalysts. The study revealed that the Co(II)-Co(III)-Co(II) cycle effectively generated the radical species that resulted in degradation of dyes. The electronic density in the highest occupied molecular orbital and lowest unoccupied molecular orbitals was also calculated to emphasize on the interaction mechanisms [322]

In short, the computational calculations and modeling provide better in-depth understanding of the various interaction phenomenon at molecular and atomic level to enable the design of efficient experimental setups. In future, significant developments are expected in the computational area which will allow the researchers to explore the dynamics, interaction energy, and structural properties at molecular

level, which will significantly improve the catalytic technologies and applications.

Conclusion and future insights

Various nanocomposite assemblies have been reported for reduction of dyes by NaBH₄. Mostly, metal nanoparticles are used for reduction of dyes and stabilized for a long time using different supporting materials. This work outlines recent modifications applied to nanocatalysts for the wastewater treatment focused on catalytic reduction reaction of organic dyes, i.e., nitrophenols, methylene blue, Congo red, and methyl orange. Further work can be preceded in the same field but slightly different dimensions by devising methods that involve useful ways for fabrication of metal nanoparticles and maintenance of their activity for a long time. Researchers need to come up with cost-effective ways of synthesizing nanocatalysts used for reduction of dyes by utilizing economic and easily available resources. Such catalysts should be reusable and eco-friendly. This review just addresses the catalytic reduction of dyes by NaBH₄ and recent applications in this area, but there is a dire need to develop new methods for the treatment of wastewater contaminants. Furthermore, no significant literature has been reported on the catalytic mineralization of toxic dyes (which is more desirable than mere decolorization) in the presence of NaBH₄ reducing agent. However, photocatalytic

activities have been reported on various materials for mineralization of several toxic dyes. The applicability of nanocatalysts for water treatment is constrained by different technical problems that require further investigation, from catalytic improvement to reactor design and method optimization. Different catalytic schemes should be employed for the reduction of dyes from wastewater so that water should be cleaned before disposal to water bodies.

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Author contributions

MN and AR conceptualized current study and reviewed literature. MI and SN performed data analysis, checked and drafted manuscript. AR, AH, and JH reviewed manuscript and provided their expert review. All author contributed to current article and approved final version.

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Declarations

Conflict of interest The authors declared that they have no conflict of interest.

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