Role of nanomaterials in catalytic reduction of organic pollutants

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Developing innovative technologies for the effective treatment of wastewater containing organic pollutants is of extreme importance across the globe. The organic pollutants such as dyes and nitrophenols are the common hazardous pollutants known for their adverse effects on humans and aquatic organisms. Various methods have been used for the removal of organic pollutants from wastewater but they suffer limitations such as high cost, time consuming removal process and production of sludge or toxic by-products. In recent years, chemical reduction method is becoming popular for removal of organic pollutants using various nanomaterials as catalysts. Nanomaterials show great potential for removal of organic pollutants due to large surface area which provides high catalytic activity. In the present review, current studies on catalytic reduction of organic pollutants (dyes and nitrophenols) using four different types of nanomaterials specifically carbon nanotubes, silica, metal oxide and chitosan polymer based have been explored. The factors affecting the catalytic process and mechanism of catalysis is explained in detail.In addition, a critical discussion about the pros and cons of each nano-catalyst have also been included for developing better understanding of the choice of catalyst.

Keywords: Catalysis, Catalytic reduction, Nanomaterials, Organic pollutants, Wastewater treatment

Introduction

Water is such an important element in our lives that needs no explanation to prove its significance. It is part of our day-to-day activities and its most vital need is in quenching our thirst which makes its purity equally important, as polluted water can cause water borne diseases which can be even more deadly. The current situation of the water bodies is considerably poor. The main reason of this condition is the increasing industrialisation. To overcome this situation, we need to find a solution to reduce the pollution caused by release of toxic and non-biodegradable waste materials into the water bodies. Pollution is rising at an alarming rate has caused harm to the lives of human beings and aquatic species too. The most important topic of research for the researchers is to reduce this pollution level as fast as we can and as soon as possible. These pollutants include agricultural wastes, pesticides and sewage effluents, but the major contributor to this water pollution is industrial wastes like dyes, organic and inorganic compounds, chemicals and their improper treatment before releasing them in the aquatic systems. The damage is already done, so it is high time to tighten our belts and find an excellent technique for the environmental remediation. Besides heavy metals,

the most concerning contaminants are the organic pollutants as they are non-biodegradable and are therefore persistent in the environment. Organic pollutants include pharmaceuticals, organic dyes, chemicals, pesticides, nitro containing compounds *etc*. which are deteriorating the quality of surface water, ground water as well as drinking water. So, remediation of water pollution is an urgent need. Toxicity of organic pollutants is highly dangerous as they can be carcinogenic, skin allergic and can even cause respiratory disorders[1,2]. Nitroaromatic compounds are mainly used in various industries for synthesis of pharmaceuticals, dyes, pigments, explosives *etc*. Nitrophenols have many negative impacts on human body as they cause irritation in nose, throat or lungs. They can penetrate our skin and can even cause problem in breathing. They can damage kidney, liver and central nervous system of human beings. Due to their environmental stability and non-biodegradability, their removal from water is difficult by the traditional water treatment methods. After knowing the toxic effects of nitrophenols the Environmental Protection Agency (EPA) has classified it as the primary pollutant and set its maximum permissible limit in natural water upto 10 ppb[3]. Dyes are another major water pollutant. They are mainly used to impart color to the fabrics, cosmetics, food, pharmaceuticals *etc*. They are highly hazardous and

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can also cause allergic skin reactions. Some dyes can even be carcinogenic. So, their impact is visible on not only humans, but also on marine animals and even on the cattle, as they are dependent on environmental sources for water and makes their removal a high prioritized one[4]. This review focuses on the removal of two types of organic pollutants, dyes and aromatic nitrophenols.

There are many conventional methods like adsorption[5], reverse osmosis[6], ion exchange[7], coagulation[8], electrochemical[9], chemical oxidation[10] and catalytic reduction which have been already introduced to remove these waste products. But, limitations like high costs, low efficiency, *etc.* resulted in development of new techniques. Adsorption technique employed for purification of water is really efficient but requires such adsorbents which can work efficiently in any environmental conditions. Then, absorbent disposal is also a matter of concern. Reverse osmosis is an expensive technique, it also destroys most of the minerals of water and requires high-pressure conditions. Ion exchange method is used to remove soluble impurities or ions of water and this method is sensitive to different pollutants. Coagulation is another method widely used for this purpose but due to production of huge amount of sludge, its application is limited. Chemical methods are harmful as they introduce toxicity in water. Oxidation is one of the methods to treat polluted water in which oxidants like H_2O_2, O_3, ClO_2 are used. Advanced oxidation processes can oxidise organic pollutants to inorganic CO_2 efficiently but the major drawback is the incomplete degradation of the by-products[1,11]. Among all, catalytic reduction method has several advantages over the conventional methods as this method leads to minimal chemical waste production, it is cost and energy efficient, and does not produce toxic by-products or sludge. On the other hand, in conventional methods, toxic organic solvents are used coupled with expensive instruments. Formation of secondary pollutants and production of sludge and hazardous by-products is another limitation of the conventional methods. So, overall catalytic reduction method is cleaner and safer[12]. The catalytic reduction method is discussed as this method helps to reduce pollution to some extent by reducing toxic organic pollutants to non-toxic products.

There are numerous catalysts that have been used for this purpose, but they suffer certain limitations as their removal is time consuming, required in large amounts

and exhibit reduced catalytic activity. Nowadays, nanomaterials in the form of nanoparticles, nanocomplexes, nanoclusters, nanoshells, nanocomposites have emerged as an excellent alternative to reduce pollution from aquatic bodies. Due to their small size, nanomaterials have large surface area and have high reactivity and thus, they are used as a catalyst for catalytic reduction, decomposition or degradation of pollutants from water bodies. Nanomaterials have optical, thermal, mechanical, structural and morphological properties which makes them a good option for many environmental applications[13]. Using them for reduction of organic pollutants is highly advantageous to reduce their damaging impact on environment. So, the nanomaterials can be exploited as catalysts making them apt candidates owing to their large surface area, high catalytic tendency and ease of surface modification. Moreover, they can be reused and are required in small quantities. Although various types of noble metal nanoparticles such as gold, silver, copper *etc.* were used as nanocatalysts for the catalytic reduction of organic pollutants, their high cost restricted their use at large scale[14].Hence, the need of alternative nanomaterials with better potential and low cost is still under study by researchers. Recently, various types of nanomaterials like metal, metal-oxides[15], carbon nanotubes[16] and polymer-based nanomaterials[17] are becoming popular due to their low cost and easy synthesis as well as modification. They have been used earlier to remove ground water contaminants like dyes, pharmaceutical drugs, organic pollutants, pesticides, nitrates *etc.*

In light of the above discussion, a literature survey based on recent studies exploring carbon nanotubes, silica, metal oxide and chitosan polymer-based nanomaterials as nanocatalysts for the catalytic reduction of organic pollutants specifically dyes and nitrophenols is discussed in this review.

Detection of organic pollutants is another major concern and for this various singular and hyphenated techniques such as UV-visible spectroscopy, GC-MS, LC-MS, HPLC *etc.* have been employed. Although hyphenated techniques give precise results but they are quite expensive and need of organic solvents and complex procedures make them less economical. Among them UV-visible spectroscopy is the simplest and commonly used detection technique for organic pollutants. It is easy to use, does not require organic solvent, gives fast and accurate results and less expensive as compared to other techniques. Its

absorbance range covers most of the organic pollutants. Further, UV-visible spectroscopy as detection technique[18] has been discussed too.

Organic Pollutants

Organic pollutants which include synthetic dyes, aromatic nitro compounds, benzene hydrocarbons, polychlorinated biphenyls require sudden treatment as even a short-term exposure with such toxic pollutants causes headache, fatigue, *etc*. These problems can be because of inhalation or skin contact with these pollutants. Nitro aromatic compounds owing to the presence of nitro groups are even found to be carcinogenic and mutagenic. The sources of the pollutants are hereby discussed.

Dyes

Water-soluble dyes released from the industries without any treatment are of major concern. Industries include rubber, leather, plastic, textile, cosmetics, paper industries that use various dyes with different chemical structure, color, and properties according to their respective applications. Even food processing industries use dyes to enhance color of their products, but unfortunately add to the toxic effluents in the water bodies enhancing the water pollution. Dyes are designed to be fade resistant, hence serves as a major limiting factor in dye removal. Conventional techniques cannot degrade or remove these synthetic dyes because of their solubility and resistance to fading. Some of the examples of synthetic dyes include methyl orange, methylene blue, methyl red, *etc*. There are many physical, chemical and biological methods for degradation, reduction or removal of these synthetic dyes from water but they have several limitations which are discussed in the next section. Therefore, catalytic reduction has gained tremendous attention as for nanocatalytic reduction of dyes

Aromatic nitro compounds

Nitrophenols are commercially used by many industries such as paper, textile, pharmaceutical, pesticides, petroleum and also by explosives manufacturing industries.Aromatic nitro compounds such as 2-nitrophenol, 4-nitrophenol are potentially carcinogenic. Their solubility and stability in the aqueous medium makes its removal from the aquatic systems extremely difficult. Therefore, nanocatalysts for the reduction or degradation of aromatic nitro compounds owing to the excellent properties of nanomaterials[14,19] are being discussed.

Methods for removal of organic pollutants

There are various methods like physical, chemical and biological methods for treatment, degradation, removal and reduction of pollutants from water.

Physical treatment

Physical methods include adsorption, membrane filtration, ion exchange technique, *etc*. Adsorption is one of the most common and efficient technique where adsorbate molecule (pollutant) gets adsorbed onto the surface of adsorbent. It is a time-consuming process and removal of the pollutants from the aqueous medium is also incomplete. In addition to adsorbent, setup for the management of adsorbed pollutant is also needed which makes the use of this technique less frequent. Another simple and economically benign process is coagulation flocculation process that requires chemicals to convert pollutants in agglomerated form, with sedimentation being used for their recovery. Sludge formation, its handling and disposal is one of the major disadvantages of this process. Ion exchange technique employs cationic and anionic resins for separation of pollutants from water in which exchange between ions and pollutants takes place, but it needs continuous monitoring. It is important to note that after a certain time, chemical treatment is needed for regeneration of resins. Reverse osmosis is another kind of filtration technique, while membrane filtration techniques include nanofiltration and ultrafiltration. In all these techniques, membranes are made up of varieties of polymer with different pore sizes for removal of contaminants from water. The maintenance and lifetime of membranes makes this technique expensive. So, overall, each physical method has advantages but also disadvantages associated with it like sludge formed has the pollutants in more concentrated form so, its handling and disposal in an appropriate manner is highly challenging. In addition to it, expensive membranes and setup for managing adsorbed pollutant is another drawback for employing physical methods.

Biological treatment

In biological treatment, a vital role is played by microorganisms. This method can be employed in three ways, aerobic, anaerobic, and a combination of both anaerobic-aerobic. Aerobic as the name says, in presence of oxygen and water already has significant amount of dissolved oxygen in it so, degradation of the organic pollutants present in aqueous systems is done by already present dissolved oxygen and by

microorganisms. Anaerobic treatment makes use of sealed tank and converts the organic waste to CH_4 and CO_2. The production of toxic compounds in either aerobic or anaerobic treatment applies sequential anaerobic-aerobic treatment as an alternative. This method is easy and energy efficient but time consuming. Also, there are many dyes and organic pollutants which cannot be degraded by this treatment. Another limitation involves its dependency on factors like oxygen level, temperature, pH and sufficient nutrients.

Chemical treatment

This treatment involves the use of chemicals, like in precipitation method, chemicals such as sulphides, carbonates and hydroxides on reaction with contaminants convert them into insoluble precipitate which agglomerates and leads to formation of sludge. One popular method is oxidation in which degradation of contaminants is done by oxidising agents like O_3, H_2O_2 and Cl_2. This process involves the generation of free radicals ($^.OH$, O_2^-) that are highly reactive and thus, kills the pollutants present in water. Ozone is a better oxidising agent than H_2O_2 and Cl_2 because of its higher oxidation potential, but it has short half-life so it is costly to supply continuous ozone. Oxidation processes like AOPs (Advanced Oxidation Process) and Fenton Reagent [H_2O_2-Fe(II)] are widely used for treatment of polluted water. However, formation of large amounts of sludge is a major limitation of Fenton process. Electrochemical oxidation or reduction processes are also employed but the correct selection of electrode with the appropriate potential, electrode fouling, expensive synthesis of electrodes and setup are the points that should be kept in consideration for this method.

All the discussed methods have their own drawbacks like high cost, high consumption of energy, expensive setups, treatment and disposal of sludge, chemical usage, *etc*. An alternative approach is catalytic reduction of these pollutants by nanomaterials. This approach has gained attention as it is simple, easy, cost effective, requires shorter period of time, and have high efficiency. In this contaminants are reduced to less toxic species with the help of $NaBH_4$ as reducing agent and so, it is safe, economic and efficient. Moreover, nanomaterials provide large surface area which facilitates the catalytic reaction.

Catalytic reduction

Catalytic reduction is a process in which toxic organic pollutants can be removed by converting them into some less toxic substance with the help of catalyst in presence of a reducing agent like $NaBH_4$. The advantage of using this method is that the product obtained is also useful. For example, 4-nitrophenol is an organic pollutant which can be reduced to 4-aminophenol with the help of a catalyst. The 4-aminophenol can be further utilized in synthesis of medicines. So, this method is a green alternative of other methods. Catalytic reduction of organic pollutants can be achieved *via* homogenous or heterogeneous catalysis. However, the heterogeneous catalysis is becoming more popular due to its high selectivity and easy separation from solution. Apart from this, the catalytic reduction method offers many advantages as listed below:

- High efficiency due to low energy consumption
- Product formed is less toxic and environmentally friendly
- Easy separation of catalyst
- Low cost and safer
- Reusability of catalyst
- No formation of sludge or toxic by-products
- Process occurs under normal experimental conditions[14,19-21].

Analytical techniques used for analysis of organic pollutants

The various techniques are employed for monitoring catalytic reduction of pollutants such as gas chromatography (GC), High pressure liquid chromatography (HPLC), Thin layer chromatography (TLC) and UV-Visible Spectrophotometry (UV-vis). The use of GC is limited to volatile samples only and the gas used should be pure. TLC is easy to perform and cost effective but environmental conditions can cause error in results as it is performed in open system.

UV-visible Spectrophotometryis an efficient technique as it requires no external solvent for analysis. The monitoring of reaction is done through absorption spectra. As absorption spectra is unique for every compound, which makes this analysis easier. For example, the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as reducing agent involves the formation of 4-nitrophenolate ion in the first step which changes the color from light yellow todark yellow and after reduction by nanocatalysts converts 4-nitrophenolate ion to 4-aminophenol accompanied by change in color from dark yellow to colorless. This causes variation in the absorption spectrum and can be clearly analysed. As both nitrophenol and aminophenol are active in the UV-

visible region, ongoing reduction reaction can be monitored by measuring absorbance at maximum absorbance wavelength of the particular compound. Absorption peak of the reactant decreases as the reaction advances into product and completely disappears at the end of the reaction which can also be marked by appearance of absorption peak of product. Nanocatalyst is taken in small amount only so that if there is any peak of nanomaterial which is coinciding with wavelength of nitrophenol, the effect of it can be considered as null because of its small quantity[18,19,21].

Factors affecting the catalytic process

There are various factors which influences the catalytic process such as temperature, amount of catalyst and reducing agent *etc*, as discussed below:

Temperature

Temperature is one of the important factors which significantly affect the rate of catalytic reduction of contaminants. Rate of catalytic reduction increases with the increase in temperature in presence of nanocatalysts for reduction of nitroarenes. But this increase in the rate of reduction was observed within a particular temperature range, for example, for 4- nitrophenol, rate of catalytic reduction with Ag-PSp (NIPAM) core-shell microgels increases for a temperature range of 15-25°C and further temperature rise causes the rate to decrease. Hence it also depends on the catalyst used.

Amount of catalyst and reducing agent

As the term nanocatalyst itself implies nanomaterials required in small amount. Owing to the large surface area to volume ratio, nanomaterials provide a large surface or a large number of surface reactive sites are available for the reaction to occur. This enhances the reactivity of reduction. Therefore, a small amount of nanocatalyst is required for catalytic reduction of contaminants in order to decrease water pollution. As the amount of nanocatalyst increases, rate of reduction of nitro aromatic compounds increases owing to the increase in the number of catalytic or active sites available for reduction. Similarly, the amount or concentration of reducing agent like $NaBH_4$ also matters in the catalytic reduction of organic pollutants. Several types of nanomaterials like silica, chitosan, metal oxide and carbon nanotubes based have been used by researchers for this purpose which is part of this review[22,23].

General Mechanism of catalytic reduction

The mechanism of catalytic reduction of organic pollutant involves the reaction between organic pollutant, reducing agent and a catalyst. The general mechanism of dyes and nitrophenols is discussed in detail as given below:

Catalytic reduction of dyes

In the catalytic reduction of dyes, first the dissociation of reducing agent $NaBH_4$ takes place which yields Na^+ and BH_4^- ions where BH_4^- acts as source of hydrogen. Congo red dye (taken as an example to explain the general mechanism of dye reduction) molecules along with the BH_4^- ions gets diffused from the aqueous media and gets adsorbed to the surface of nanocatalyst. BH_4^- acting as electron donating species transfers its electrons to the nanoparticle and releases hydrogen which attacks on the congo red molecules. Complete reduction of congo red is indicated by color being converted to colorless. Basically, it goes from being fade due to conversion of -N=N- bond to -HN-NH- bond and then ultimately becomes colorless because of breakage of -HN-NH- bond as shown in (Fig. 1). Then, the product separates out from the surface of nanocatalyst[24].

Catalytic reduction of aromatic nitro compounds

This could be explained by Langmuir-Hinshelwood adsorption model as shown in (Fig. 2). According to this model all the reactants, aromatic nitro compound and reducing agent $NaBH_4$ gets adsorbed on nanoparticle surface. $NaBH_4$ dissociates into ions Na^+ and BH_4^- where BH_4^- acts as an electron donating
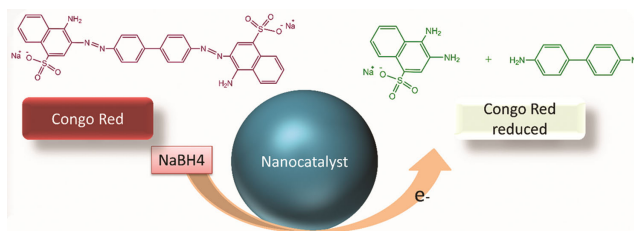

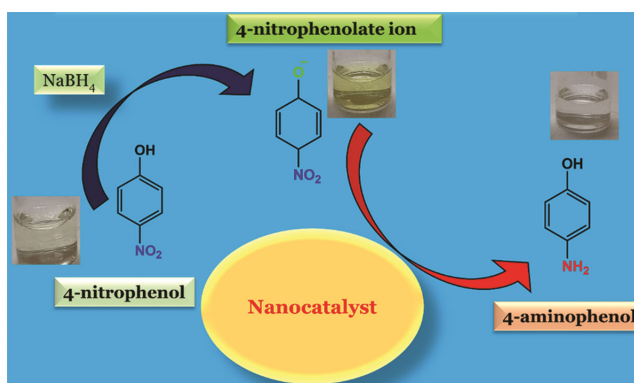Fig. 1 — Catalytic reduction mechanism of Congo red dye

Fig. 2 — Catalytic reduction mechanism of 4-nitrophenol

species which firstly converts 4-nitrophenol to 4-nitrophenolate ion and then finally gets reduced to 4-aminophenol in presence of a catalyst. During this due course of reaction, hydrogen is also released by $NaBH_4$ which not only increases the rate of reaction but also lowers induction time to activate nanoparticles by reconstructing its surface. By this H-flux, impurities on nanocatalyst surface are removed which consequently increases the number of sites on the nanocatalyst surface for the reaction to happen. Catalytic performance of nanomaterials makes this method fast because in the absence of NPs, this reduction is limited by $NaBH_4$[25].

Catalytic reduction of organic pollutants using different Nanomaterials

Catalytic reduction is a popular method for conversion of toxic organic contaminants into non-toxic or useful product. Nowadays, use of nanomaterials as nanocatalyst is attracting many researchers due to advantages such as large surface area, fast reaction rate and less amount of catalyst required. Various types of nanomaterials of carbon, metal, metal oxide, silica and polymeric have been used as nanocatalyst. Carbon based nanomaterials includes mainly two types, graphene and carbon nanotubes. Carbon nanotubes are rolled graphene sheet in cylindrical form. Based on number of rolled graphene sheets, carbon nanotubes can be further classified as single walled carbon nanotubes (SWCNT), if it contains only one sheet, double walled carbon nanotubes (DWCNT) if it contains two sheets and multi walled carbon nanotubes (MWCNT) if it contains multiple graphene sheet. Their small size and unique structural properties enhance their applications in various fields. Silica or silicon dioxide is present in abundance on earth's crust so is of low cost. It is inert, biocompatible and non-toxic, therefore widely used in biomedical applications and in electronic industries. Silica based nanomaterials including silica nanoparticles and its nanocomposites with metals or polymers have also been used in the treatment of wastewater. Metal oxide based nanomaterials include nano titanium oxide (TiO_2), nano ferric oxide (Fe_3O_4), nano zinc oxide (ZnO), nano copper oxide (CuO) *etc.* due to large surface area have been used in various industrial and environmental applications. Due to the presence of charge on the metal oxide nanoparticles they can attract the ionic organic pollutants easily which makes them good catalysts. They are cheap and can be easily synthesized. Polymer based nanomaterials

includes chitosan, cellulose, *etc*. Cellulose is the most abundant biopolymer, which is a polysaccharide and contains many hydroxy functional groups. Chitosan is another biopolymer which is obtained from the deacetylation of chitin (anatural biopolymer, present in the exoskeleton of shrimps, crabs, *etc*.) hence, it is cheap and environment friendly. Chitosan also has antimicrobial and antibacterial properties. Due to its non-toxic, biodegradable and biocompatible nature it is widely used in drug delivery and other biomedical applications. Chitosan has amine and hydroxyl functional groups which facilitates its applications in many fields of science including environment remediation[20]. In this review four types of nanomaterials namely, carbon nanotubes, silica, metal oxide and chitosan based are focussed and their use as catalyst is described as given below:

Catalytic reduction of organic contaminants by carbon nanotubes-based nanomaterials

Carbon nanotubes including single walled carbon nanotubes (SWCNT) and multi walled carbon nanotubes (MWCNT) are most common. They have huge surface area, electrical and mechanical properties which enhances their catalytic activity. Further modification with metal nanoparticles and polymers facilitates easy attachment with pollutants. SWCNT also exhibit antibacterial properties which makes it more applicable for environment remediation. MWCNT not only provide large surface area for catalytic activity but also behave as good catalytic carrier. Their modification with metals further promotes the catalytic activity. Catalytic reduction of organic pollutants using carbon nanotubes-based nanomaterials was done by many researchers such as, Bhaduri *et al.*, (2018) synthesized carbon nanotube based composite material *i.e.*, Ag-Fe_3O_4-SWCNT and used it for catalytic reduction of aromatic nitrophenols, o-nitrophenol, p-nitrophenol, 2-methyl-p-nitrophenol and methyl orange dye. The composite exhibited excellent catalytic activity as indicated by rate constants obtained for o-nitrophenol, p-nitrophenol, 2-methyl-p-nitrophenol and methyl orange were 2.83, 1.74, 1.80 and 0.88 s^{-1} g^{-1}, respectively[26]. Similarly, Li *et al.* (2020) synthesized Cu nanoparticles supported on CNT. The size of synthesized nanoparticles was 4-10 nM and were used as nanocatalyst for catalytic reduction of 4-nitrophenol. The result revealed that complete catalysis occurred in 80 min at 45°C. The rate constant obtained was 0.0532 min^{-1} [28]. Similarly,

Deshmukh and co-workers synthesized silver-supported polyaniline/MWCNT nanocomposites and used it for catalytic reduction of 4-nitrophenol. The synthesized nano-particles were crystalline with face-centred cubic (FCC) lattice and the size of nanoparticles was found in range of 15-20 nM. The nanoparticles showed fast catalysis within 240s with only 1 mg of catalyst and rate constant obtained was 5.4×10^{-3} s^{-1} [30]. The catalytic reduction of organic contaminants using different nanocomposites of carbon nanotubes are reported in (Table 1).

Catalytic reduction of organic contaminants by silica-based nanomaterials

Silica being inert and abundant in nature is used in reduction of organic pollutants present in water. Silica based nanomaterials due to extremely small size, enormous surface area, high thermal stability, uniform pore size and large pore volume makes them highly applicable in the catalytic field. All these properties specially their inertness provides a protective shell for the metal catalyst which generally agglomerates due to charge and thus makes a good catalyst. Catalytic reduction of organic pollutants using silica-based nanomaterials was studied by various researchers as recently, Mohammadi and Sheibani synthesized $Fe_3O_4@SiO_2-Ag$ magnetic nanocatalyst using safflower extract and used it for catalytic reduction of 4-nitrophenol. The shape of synthesized nanoparticles was found to be quasi-spherical and the size obtained using TEM was 10-14 nM. The 1 mg of nanocatalyst showed catalysis of 4-nitrophenol within 4 min, methylene blue

in 50 s and methyl orange in 60 s at room temperature. The rate constant obtained for 4-nitorphenol, methylene blue, and methyl orange were 0.756 min^{-1}, 0.09 s^{-1}, and 0.064 s^{-1}, respectively[33]. Similarly, Korobeinyk and co-workers synthesized three nanocomposites of noble metal nanoparticles on fumed silica namely, Pt/SiO_2, Ru/SiO_2 and Au/SiO_2 nanocomposites. The 2-nitrophenol was chosen as model organic pollutant to study the catalytic activity of nanocomposites. The nanocomposites showed complete catalysis of 2-nitrophenol within 15 min at room temperature and the rate constants obtained were 1.3×10^{-1}, 8.2×10^{-1}, and 8.6×10^{-1} min^{-1} for Pt/SiO_2, Ru/SiO_2 and Au/SiO_2 nanocomposites respectively[41]. The catalytic reduction of organic contaminants using different nanocomposites of silica are reported in (Table 2).

Catalytic reduction of organic contaminants by metal oxide based nanomaterials

Metal oxide based nanomaterials also have high surface area and catalytic activities. Their easy fabrication and selectivity towards particular pollutants makes them good catalyst. There are various types of metal oxide nanomaterials including magnetic nanoparticles, CuO, ZnO nanoparticles, *etc*. have been used as catalysts for reduction of many organic pollutants. Among them magnetic nanoparticles and its nanocomposites are getting more popular due to their easy synthesis and separation process. Although metal oxide based nanomaterials are excellent catalysts but their agglomeration over a time span increases their size to macro level and

Table 1 — Catalytic reduction of organic contaminants by carbon nanotubesbased nanomaterials

Catalyst	Morphology, Size	Organic pollutants	Temperature (°C)	Reactiontime (min)	Reaction rate constant, k (min^{-1})	References
Ag-Fe$_3$O$_4$-SWCNT	-	o-nitrophenol	25	7	2.83[#]	[26]
		p-nitrophenol		10	1.74[#]	
		2-methyl-p-nitrophenol		10	1.80[#]	
		Methyl orange		-	0.88[#]	
Ag/MWNTs nanocomposites	Crystalline	4-nitrophenol	25	10	-	[27]
Cu nanoparticles supported on CNT	4-10 nM	4-nitrophenol	45	80	0.0532	[28]
Poly(propylene imine) dendrimer stabilized silver nanoparticles on MWCNT	14.07-69.24 nM	4-nitrophenol	-	33	16.94x10^{-2}	[29]
Silver-supported polyaniline/MWCNT nanocomposites	FCC 15−20 nM	4-nitrophenol	RT	240*	5.4×10^{-3}[**]	[30]
SnO$_2$-CNT nanohybrids	Crystallite ~35.2 nM	4-nitrophenol,	RT	16	-	[31]

[#]$s^{-1}g^{-1}$, *s^{-1}, **s^{-1}

hence their catalytic performance reduces. This problem was resolved by their modification with polymers and other supporting materials which improves their stability as well as catalytic properties. Various metal oxide based nanoparticles and nanocomposites showed good catalytic activity and hence used for the reduction of organic pollutants. Catalytic reduction of organic pollutants using metal oxide based nanomaterials was studied by T. Kamal, who synthesized agar biopolymer hydrogel supported CuO nanoparticles and used it for catalytic reduction of three types of nitrophenols namely, 4-nitrophenol (4-NP), 2,6-dinitrophenol (2,6-DNP) and 2-nitrophenol (2-NP). The surface of synthesized nanoparticles was

found to be rough with bright spots and size obtained was 92 ± 15 nM. The 0.22 g of nanoparticles showed good catalytic activity as catalysis of 4-NP, 2,6-DNP and 2-NP completed within 10, 7 and 7 min at room temperature with rate constants 0.401, 0.291 and 0.306 min^{-1}, respectively[44]. Similarly, Bakhsh et al. synthesized cellulose acetate-ferric oxide nanocomposite and used it for catalytic reduction of 4-nitrophenol and methyl orange dye. The nanocomposite showed complete catalysis of 4-nitrophenol, methyl orange dye within 13 and 7 min and the rate constants obtained were 4.77×10^{-3} and 8.58×10^{-3} s^{-1}, respectively[56]. Catalytic reduction of organic contaminants using different nanocomposites of metal oxides are reported in (Table 3).

Table 2 — Catalytic reduction of organic contaminants by silica based nanomaterials

Catalyst	Morphology, Size	Organic pollutants	Temp. (°C)	Reaction time (min)	Reaction rate constant, k (min^{-1})	References
$Ag@SiO_2$ nanoparticles	spherical, 80-500 nM	4-Nitrophenol, Rhodamine-B	RT	11	0.1868, 0.4359	[32]
$Fe_3O_4@SiO_2$-Ag Nanocomposite	quasi-spherical, 10-14 nM	4-nitrophenol, Methylene blue, Methyl orange	RT	4 50* 60*	0.756, 0.09**, 0.064**	[33]
$Fe_3O_4@SiO_2$/EP.EN.EG@ Cu nanoparticles	spherical, 20 nM.	4-nitrophenol	50	15	$3.2 \times 10^{-3**}$	[34]
$Fe_3O_4@SiO_2$-Tet-Cu(II)	spherical, 42 nM	4-nitrophenol, 2,4-dinitrophenilhydrazin, Methylene blue, Nigrosin	RT	120* 71* 10* 30*	-	[35]
$Ir/IrO_2@Fe_3O_4$ core/ SiO_2 shell nanocomposites	-	4-nitrophenol, 4-nitroaniline and 2-nitroaniline	RT	3 3 4	1.32, 1.34 and 0.92	[36]
SiO_2 caped Fe_3O_4 nanostructures	aggregated and semi-spherical, 16 nM	4-nitrophenol		4	$9 \times 10^{-3*}$	[37]
Gold Nanoparticles Grafted Mesoporous Silica (Au/SiO_2)	spherical, crystalline FCC, ~6-10 nM	4-Nitrophenol	Ambient Temp.	20	-	[38]
Mesoporous silica nanoreactor with polymer poly(2-(dimethylamino)ethyl methacrylate)	rod-like shape pore diameter (5.7 nM)	4-nitrophenol	-	50	-	[39]
Nickel silicate and nickel silicate/nickel composite nanotubes	nanospheres and nanorods 16.3 nM	4-nitrophenol	-	12	0.437	[40]
Noble metal nanoparticles on fumed silica Pt/SiO_2, Ru/SiO_2 and Au/SiO_2 nanocomposites	5-19 nM	2-nitrophenol	RT	15	1.3×10^{-1} 8.2×10^{-1} 8.6×10^{-1}	[41]
Pt nanoparticles with porous silica	hexagonal and/or rectangular 3.8 nM	4-nitrophenol Methylene blue	-	- -	0.321, 0.512	[42]
Silica cubic particles decorated with silver nanoparticles	100-200 nM	4-nitrophenol	RT	150*	$30 \times 10^{-3**}$	[43]

**s^{-1}

Table 3 — Catalytic reduction of organic contaminants by Metal oxide based nanomaterials

Catalyst	Morphology, Size	Organic pollutants	Temp. (°C)	Reaction time (min)	Reaction rate constant, k (min^{-1})	References
AG-CuO nanoparticles	rough surface with bright spots, 92 ± 15 nM	4-nitrophenol 2,6-dinitrophenol 2-nitrophenol	RT	10 7 7	0.401, 0.291, 0.306	[44]
Ag/CuO nanocomposite	spherical, crystalline,	4-nitrophenol	-	30	-	[45]
Ag@Cu$_2$O nanocomposite Ag@Cu$_2$O-Au nanocomposite	-	4-nitrophenol	-	44 5	-	[46]
Ag/C/ZnO nanocomposites	agglomeration.	4-nitrophenol Methylene blue Rhodamine-B	-	7 80* 140*	0.286 - -	[47]
Ag-Cu@ZnO bimetal nanocomposite	Spherical 12 nM (AgNP)- 25 nM (CuNP)	4-nitrophenol Methylene blue Rhodamine B	RT	10* 6* 8*	-	[48]
Ag/Fe$_3$O$_4$/RGO nanocomposites	spherical, 22 nM	4-nitrophenol Methylene blue Methyl green Methyl orange	RT	53* 98* 84* 76*	-	[49]
Ag doped Fe$_3$O$_4$ embedded ZnO nanocomposites, (I) Ag/ZnO (AZ), (II) Ag/Fe$_3$O$_4$ (AF), Ag/ZnO/Fe$_3$O$_4$ (AZF)	Sphere, Nano cubes and tubular structures, Granules	4-nitrophenol	-	3, 4 & 2	-	[50]
Ag/RGO/TiO$_2$ nanocomposite	GO sheet was decorated with TiO2 aggregates, 30 nM	4-nitrophenol Congo red Methylene blue	303 K	195* 116* Immediately	-	[51]
Ag@SrTiO$_3$ nanocomposite	nanosheets-assembled flower-like structure, 2 nM	4-nitrophenol	293K	7	0.536	[52]
Au/γ -Al$_2$O$_3$ nanoparticles	spherical, 8 nM	4-nitrophenol	25 C	25	1.2×10^{-4}	[53]
Au-Pt@TiO$_2$ nanocomposite	spherical, ~54 nM	4-nitrophenol Methylene blue Congo red	-	8*, 6*, 5*	-	[54]
Au/CaCO$_3$ nanocomposite	crystalline, 6.0 nM	4-nitrophenol	RT	3	1.0750	[55]
Cellulose acetate-ferric oxide nanocomposite (CA/Fe$_2$O$_3$)	Crystalline,	4-nitrophenol Methyl orange	-	13 7	$4.77 \times 10^{-3**}$ $8.58 \times 10^{-3**}$	[56]
CeO$_2$ nanoparticle	rhombohedron, 17 nM	4-nitrophenol	RT	60*	-	[57]
Cu/Al$_2$O$_3$ nanoparticles	spherical, nearly 5-17 nM	2,4-dinitrophenylhydrazine Methylene blue Congo red	RT	30* 33* 164*	-	[58]
CuO nanoparticles	100-200 nM	Methylene Blue	RT	10	0.345	[59]
CuO nanoparticles		Acid red, Acid green, Methylene blue, Rhodamine B Solochrome black-T				[60]
CuO nanoparticles	spherical, 22 ± 1.5 nM	4-nitrophenol	25 C	20	-	[61]
CuO nanosheets (A$_1$, A2, A3)	13-15 nM	4-nitrophenol	-	5	0.168 0.275 0.264	[62]
CuO NPs/clinoptilolite	spherical, 10-20 nM	4-nitrophenol Methylene blue Rhodamine B	Ambient Temp.	150* Immediately 60*	-	[63]

(*Contd.*)

Table 3 — Catalytic reduction of organic contaminants by Metal oxide based nanomaterials (*Contd.*)

Catalyst	Morphology, Size	Organic pollutants	Temp. (°C)	Reaction time (min)	Reaction rate constant, k (min^{-1})	References
CuO nanostructures (A) CuOW; (B) CuOA; (C) CuOC; and (D) CuOT	nanorods, spherical, nanostars, banoflowers	4-nitrophenol		34 26 20 28	$4.5×10^{-2}$, $6.0×10^{-2}$, $7.5×10^{-2}$, $4.9×10^{-2**}$	[64]
CuO/Cu$_2$O hybrid nanowires	nanowires, 27 nM	4-nitrophenol		4	0.5014	[65]
Cu$_2$O-Cu-CuO nanocomposite	50-100 nM	4-nitrophenol	RT	3	0.9407	[66]
CuO-PES-CA nancomposite supported Cu^0 nanoparticles i. PES-CA-CuO, ii. Cu@PES-CA, iii. Cu@PES-CA-CuO-1 iv. Cu@PES-CA-CuO-2		o, m, p-nitrophenol				[67]
Copper nickel oxysulfide nanoparticles (CuNiOS-0.6)	uniform and regular, 9-20 nM	4-nitrophenol, Methyl blue, Rhodamine-B	RT	90* 30* 60*	$70.0×10^{-3**}$ $144×10^{-3**}$ $130×10^{-3**}$	[68]
Cobalt ferrite Bismuth substituted cobalt ferrite	crystalline	4-nitrophenol	RT	2.25	-	[69]
CuAg nanoparticles on highly porous ZnO/carbon black-cellulose acetate sheets	crystalline	o-nitrophenol m-nitrophenol p-nitrophenol 2,6-dinitrophenol Methyl orange Congo red Methylene blue Rhodamine B	-	7	- - $1.9×10^{-1}$ - $9.0×10^{-2}$ - - -	[70]
CdS−TiO$_2$-based Palladium nanocatalyst	5-9 nM	4-NP 4-NA 2-NP 2-NA O-NPDA	RT	13, 6, 2, 5, 2	0.0432, 0.1808, 0.2700, 0.3015, 0.2936	[71]
Fe$_3$O$_4$-guargum nanocomposite	cubic, ~48 nM	4-nitroaniline		60		[72]
Fe$_3$O$_4$–MnO$_2$ nanocomposites i. Fe$_3$O$_4$-MnO$_2$ (PE) ii. Fe$_3$O$_4$-nO$_2$ (GA) iii. MnO$_2$ iv. Fe$_3$O$_4$	nanoflake	4-nitroaniline	25 ± 1°C	90*	$8.2×10^{-2}$, $8.0×10^{-2}$, $7.6×10^{-2}$, $2.5×10^{-2*}$	[73]
rGO-Co$_3$O$_4$ nanocomposite	aggregated and crumpled sheets on nanoparticles, 2-10 nM	4-nitrophenol	RT	60*	-	[74]
MgFe$_2$O$_4$/Ag$_3$PO$_4$nanocatalyst	spherical, 21 nM	4-nitrophenol	RT	1	3.0224	[75]
Nanocrystalline ZnO–NiO	crystalline, 8.5-10.3 nM	4-nitrophenol	RT	16-19	-	[76]
Ni(NO$_3$)$_2$ and NiO, immobilized over CeO$_2$ nanoparticle	spherical, 12 nM	4-nitrophenol	-	60, 60	0.0673, 0.0056	[77]
Pd–Fe$_3$O$_4$–Sm$_2$O$_3$–ZrO$_2$ nanocomposite	29.5 and 45.3 nM	2-nitrophenol	RT	0.17-0.6	$0.0626**$	[78]
Silver doped copper and zinc nano metal oxides i. ZnO ii. Ag/ZnO, iii. CuO & iv. Ag/CuO nanocomposites	rod, spherical, quasi-shperical, rod<10 nM	4-nitrophenol	-	3-5 3.5	-	[79]

Catalytic reduction of organic contaminants by chitosan based nanomaterials

Chitosan is a non-toxic, biodegradable and biocompatible polymer which is a green alternative as obtained from natural resources and available in abundance. Chitosan based nanomaterials due to their large surface area, and presence of additional functional groups helps in easy attachment of pollutants makes it a good candidate for the catalytic activity. Chitosan forms stable bonds with other metal nanoparticles which further improves the catalytic properties. It is cheap and environment friendly in comparison to other nanomaterials. The catalytic reduction of various organic contaminants using chitosan based nanomaterials was evaluated by different researchers as recently, Khan *et al.* (2020), synthesized Ag/ZnO-CH textile cotton supported nanocomposites and used for catalytic reduction of various forms of organic nitrophenol such as para-nitrophenol, meta-nitrophenol, ortho-nitrophenol, 2,4,6-trinitrophenol and dyes like methyl orange, congo red, and methyl red[81]. The structure of nanoparticles was hexagonal wurtzite and the size obtained was 69.32 nM ($\pm$ 10 nM). The time required

for catalysis of para-nitrophenol, meta-nitrophenol, ortho-nitrophenol, 2,4,6-trinitrophenol by 15 mg of Ag/ZnO-CH textile cotton supported nanocomposites at room temperature was 11, 29, 33, 20 min and rate constants obtained were 2.813×10^{-3}, 4.245×10^{-4}, $8.155 \times 10^{-4,}$ and 1.157×10^{-3} s^{-1}, respectively. The nanocomposite also showed good catalytic activity towards catalysis of dyes as methyl orange, congo red, and methyl red dyes were completely catalysed within 12, 11 and 16 min and rate constants obtained were 1.663×10^{-3}, 1.43×10^{-3}, and 1.577×10^{-3} s^{-1}, respectively[81]. Similarly, Khan *et al.* synthesized silver nanoparticles in chitosan hydrogel. The modified nanoparticles surface was found smooth with bright spots, and the size of nanoparticles was around 70 $\pm$ 22 nM. The nanoparticles were applied as nanocatalyst for catalytic reduction of 2-nitrophenol and acridine orange. The complete catalysis of 2-nitrophenol and acridine orange occurred within 6 min and rate constant obtained was 0.260, and 0.253 min^{-1}, respectively[95]. The catalytic reduction of organic contaminants using different nanocomposites of chitosan are reported in (Table 4).

Table 4 — Catalytic reduction of organic contaminants by chitosan based nanomaterials

Catalyst	Morphology, Size	Organic pollutants	Temp. (°C)	Reaction time (min)	Reaction rate constant, k (min^{-1})	References
Ag-γ-Fe$_2$O$_3$@CS	8.7 nM	Methyl orange	RT	200*	$2.7 \times 104^{\#\#}$	[80]
Ag/ZnO-CH textile cotton supported nanocomposites	hexagonal wurtzite structure, 69.32 nM ($\pm$ 10 nM)	p-nitrophenol m-nitrophenol o-nitrophenol 2,4,6-trinitrophenol Methyl orange Congo red, and Methyl red	RT	11 29 33 20 12 11 16	2.813×10^{-3} 4.245×10^{-4} 8.155×10^{-4} 1.157×10^{-3} 1.663×10^{-3} 1.43×10^{-3} $1.577 \times 10^{-3**}$	[81]
Asparagine functionalized chitosan magnetic nanoparticles (ACMNPs)	6.0-7.5 nM spherical as well as semi-spherical	4-nitrophenol	RT	6	0.4681	[82]
CH/CeO$_2$-Co$_2$O$_3$ nanocomposite	$\pm$50 nM. aggregation	4-nitrophenol, 2,6-diNP, 2-NP	-	9 13 12	0.4625, 0.2396, 0.2411	[83]
Chitosan-Guar gum blend Silver Nanoparticle bionanocomposite	spherical and some are triangular, 50 nM	4-nitrophenol	-	3	-	[84]
Chitosan coated cotton cloth supported zero-valent nanoparticles	crystalline, FCC, 6.92 to 7.03 nM	4-nitrophenol, Rhodamine-B, Methylene blue, and Methyl orange	-	-	0.2937, 0.3804, 0.2802, 0.1698	[85]
Chitosan-coated polyurethane sponge supported metal nanoparticles	agglomerates	4-nitrophenol	-	5	0.7923	[86]

(*Contd.*)

Table 4 — Catalytic reduction of organic contaminants by chitosan based nanomaterials

Catalyst	Morphology, Size	Organic pollutants	Temp. (°C)	Reaction time (min)	Reaction rate constant, k (min^{-1})	References
Chitosan supported palladium nanoparticles. CS/Pd-5%, CS/Pd-10% and CS/Pd-15%	spherical, ~ 2.1 nM	4-nitrophenol	Ambidient Temp	36, 22, 18	1.95×10^{-3}, 2.41×10^{-3}, $4.01 \times 10^{-3**}$	[87]
CS-TiO$_2$ nanocomposite (CS-chitosan)	small dots/nanoparticles, 28.73 nM	4-nitrohphenol, 2-nitrophenol, 3-nitrophenol and 2,6-dinitrophenol, Methyl orange, Congo red, Methylene blue, and Acridine orange	-	- 8 11 16 4 4 4 13	-	[88]
Copper nanoparticles embedded chitosan	spherical, 5 nM	4-nitroaniline, 4-nitrophenol	-	6 6	7.51×10^{-3}, $6.46 \times 10^{-3**}$	[89]
Fe$_3$O$_4$@Chitosan –AgNP nanocomposite	10.8±3.0 nM	4-nitrophenol	RT	20	0.83	[90]
Fe$_3$O$_4$@Ch-MNPs, M = Au, Pd	spherical,~35 nM	4-nitrophenol	-	3-14	-	[91]
Fe$_3$O$_4$@CS_AgNi, where CS = Chitosan Fe$_3$O$_4$@CS, Fe$_3$O$_4$@CS_Ni, and Fe$_3$O$_4$@CS_Ag	20-25 nM	4-nitrophenol	RT	10, 10, 10	0.03, 0.42, 0.56	[92]
Gold-Chitosan Nanocomposite Films	irregular shapes, 200 nM	4-nitrophenol	-	150	-	[93]
Pd@PANI-CS-Fe$_3$O$_4$nanocatalyst	crystalline	4-nitrophenol	RT	14	0.222	[3]
Silver nanoparticles/chitosan-coated cellulose filter paper	crystalline FCC, 23 nM	2-nitophenol and 4-nitrophenol	-	-	$3.9 \ 9 \times 10^{-3}$, $1.7 \ 9 \times 10^{-3**}$	[94]
Silver nanoparticles in chitosan hydrogel	smooth surface with bright spots, 70 ± 22 nM	2-nitrophenol and Acridine orange	-	6 6	0.260, 0.253	[95]

Conclusion

It is very true that with time and technology, science has given this world beautiful inventions, instruments that are so precise, and numerous kinds of machines that makes our life easier and the work is unstoppable till date but on the same hand, we are lagging in maintaining an ecological balance with the nature. Every field in science has two aspects, one is what new we are inventing and second how are we managing the wastes produced with that invention. We have done and are still doing an excellent job in discovering new things but we are creating a threatening impact on our nature. Dyes, that plays a vital role in our lives as they fill our lives with different beautiful colors but on the other hand it has now become a major pollutant that can even cause serious health issues. Similarly, 4-nitrophenols are used in industries for manufacturing drugs, insecticides, *etc.* but managing its concentration in the waste effluents has not been taken care of. The result of this careless and reckless behaviour and mindset of people has polluted various sources of water so badly that it can even take lives. This review highlights one of the efficient methods to reduce these contaminants to less toxic products which can help in decreasing the pollution level to some extent and also in increasing purity of water. Catalytic reduction of organic pollutants (dyes and nitrophenols) by nanomaterials (carbon nanotubes, silica, metal oxide based and chitosan polymer based) has been discussed as an alternative way to reduce the toxic pollutants into less toxic products. Further, different methods used for reduction of pollutants has also been discussed in brief and moreover, the advantages of catalytic reduction over other methods have been highlighted.

Conflict of interest

All authors declare no conflict of interest.

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