Chapter 7 Nanoparticles in Dye Degradation: Achievement and Confronts

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Abstract At present, the textile industries are growing very fast to meet the demand of exponentially growing population. They discharge effuent in an open environment, which is responsible for causing serious health concerns to the life forms and polluting the environment due to the presence of dye. So, it is necessary to degrade the harmful dyes from the effuent before their discharge in the surroundings. Several conventional methods are in use for dye removal such as activated carbon adsorption, ozonation, electrochemical oxidation, forward osmosis, biological degradation, coagulation, and focculation, but these methods are ineffcient in successful degradation of dye from the effuent and are also not environmentally friendly. Nowadays, nanomaterials have found a wide range of applications in different felds such as analytical, cosmetics, agriculture, electronics, and medical applications. This is due to their unique properties like small in size, large surface area, highly electrocatalytic, biocompatible, antimicrobial properties, and so on. These unique properties have attracted different researchers to use them for degradation of dyes from the effuent of various industries. This review highlights the toxicity caused by the dye-containing effuent and the mechanism of degradation of dye using nanomaterials. The chapter also emphasizes on the use of nanomaterials (nanoparticles, carbon nanotubes, nanorods, graphene sheets, and fullerene structure) for dye removal.

Keywords Dye · Nanomaterial · Nanoparticles · Graphene · Nanotube

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7.1 Introduction

A dye is a colored compound that possesses affnity to bind at specifc substrate and imparts color to that substrate. The dyes have been categorized into ionic and nonionic dyes. The ionic dyes consist of cationic and anionic dyes. These anionic dyes are further subcategorized into acidic, reactive, and direct dyes. On the other hand, nonionic dyes have been categorized into vat and disperse dyes, as shown in Fig. [7.1](#page-1-0) (Tan et al. [2015\)](#page-15-0). Presently, dyes have found a wide range of applications in papermaking, food, pharmaceuticals, cosmetics, paint, textile, and leather industries (Nautiyal et al. [2016\)](#page-14-0). To fulfll the demand of dyes in various industries, around 1.6 million tons of dyes have been produced every year. Around 10–15% of this total produced dyes are being discharged unused as effuent in an open environment (Hunger et al. [2003\)](#page-13-0). These untreated and unused dyes present in effuent are composed of harmful chemicals, resulting in environment contamination. The toxic dyes percolate to groundwater via soil fnally leading to groundwater contamination. As a result of this, these toxic dyes enter into the food chain causing serious health concerns in humans as well as in animals. These dyes are responsible for causing mutagenic, carcinogenic, and teratogenic effects in living beings (Alves de Lima et al. [2007\)](#page-12-0). So, it is necessary to treat the dyes from the effuent before their discharge into the environment.

Several methods have been reported to treat these harmful dyes such as adsorption using activated carbon (Ruhl et al. [2014\)](#page-15-1), ozonation of dyes (Punzi et al. [2015\)](#page-15-2), photocatalytic degradation of azo dyes hydrothermally (Saleh [2019](#page-15-3)), electrochemical oxidation (Gao et al. [2019\)](#page-13-1), biological treatment of textile dyes (Paz et al. [2017\)](#page-14-1), forward osmosis (Korenak et al. [2019](#page-13-2)), coagulation-focculation-based treatment of dye (GilPavas et al. [2017](#page-13-3)) using nanofltration membranes (Wang et al. [2018\)](#page-16-0), and

Fig. 7.1 Schematic diagram of classification of dyes

many more. Among all methods reported above, the activated carbon has been extensively used for the successful removal of dyes from effuent (Carrott et al. [1991\)](#page-12-1). But the drawback of using activated carbon for dye removal is that it is expensive as its production and reactivation require steam, which is maintained at high pressure, and it further increases the dye removal cost (Marsh and Rodríguez-Reinoso [2006](#page-14-2)). To make the process cost-effective, investigators have reported the use of adsorbents for dye removal, which include leaf-based adsorbents (Bulgariu et al. [2019](#page-12-2)), adsorption using palm oil (Hameed et al. [2009\)](#page-13-4), calcium biochar adsorbent derived from crab shell (Dai et al. [2018\)](#page-13-5), geopolymer paste adsorbent (Maleki et al. [2018](#page-14-3)), and palm oil-derived microcrystalline cellulose (Tan et al. [2018](#page-15-4)). The above adsorbents have been successfully used for dye removal from the effuent. As adsorption depends solely on the surface area, it is necessary to enhance surface area of the adsorbents.

This requirement can be easily fulflled using nanomaterials, especially nanoparticles. Metallic nanoparticles being small in size range from 1 to 100 nm and offer high surface area. Nowadays, nanomaterials are considered as an important candidate for adsorption of dyes due to their high surface area, presence of short intraparticle distance with respect to diffusion, pore size tunability, possess large surface area, high mechanical strength, presence of active sites, and low mass (Sweet et al. [2012;](#page-15-5) Mallakpour and Rashidimoghadam [2019](#page-14-4)). This review focuses on dye removal using nanoparticles, carbon nanotubes, nanorods, graphene, and fullerene with the amount of adsorbent used and the efficiency of dye removal.

7.2 Toxic Effect of Dye

In the textile industry, synthetic dyes have been extensively used for developing colorfast and bright hues. But the toxic nature of these synthetic dyes resulted in carcinogenic effects on humans and animals and also affects the environment. The discharge from these industries comprises of dyes along with sulfur, soaps, dye fxing agents, and other nonbiodegradable chemicals resulting in generation of toxic effuent. When this untreated effuent is discharged in open environment, it leads to clogging of soil pores, which results in decline of soil productivity, and also affects the quality of drinking water (Kant [2012\)](#page-13-6).

Another source of toxic effuent is the paper and pulp industry, which contain dyes and lignocellulose material. Their discharge imparts dark color, increase in chemical oxygen demand, and imbalances pH of water (Pokhrel and Viraraghavan [2004\)](#page-15-6). This is mainly due to the presence of dyes and other organic ligands from wood and the tannins, lignin, etc. (Lacorte [2003\)](#page-13-7). The untreated effuent is also responsible for the reduction in transparency of water affecting photosynthetic activity of aquatic plants and animals, resulting in death (Meriläinen and Oikari [2008\)](#page-14-5).

Also, effuent from the cosmetic industry is nonbiodegradable due to the presence of organic dyes, which are polar in nature (Chen et al. [2007\)](#page-13-8). So, its untreated discharge results in increase of chemical oxygen demand. Effuent-containing dyes from other industries such as paint and pigmentation also lead to serious health concerns to all life forms and the environment.

7.3 Mechanism of Dye Removal Using Nanomaterials

The dyes have been successfully removed using a variety of nanomaterials via photodegradation. The process of photodegradation takes place on surface of nanomaterial in the presence of ultraviolet light, which excites electrons from valence band to conduction band leaving behind holes. The potential at valence band $(h⁺)$ is positive, which can easily produce hydroxyl radicals (OH) on the surface of the nanomaterial. On the other hand, potential at conduction band (e[−]) will be negative, which is helpful in reduction of oxygen. The oxidizing nature of OH radical will degrade dye present in the vicinity of nanomaterial surface as illustrated in Fig. [7.2](#page-3-0) (Khataee and Kasiri [2010\)](#page-13-9). Photocatalysis of dye was also reported with SnO₂ nanotube. The mechanism is nearly the same as discussed above in the case of nanoparticle. When nanotubes are exposed to light, photon is absorbed, and an electron is ejected from valence band of the nanotube, which moves toward conduction band leaving behind a hole in valence band. During this, holes start migrating toward conduction band, and electrons start moving to valence band. This movement will increase charge transfer leading to oxidation and reduction of oxygen and hydroxyl molecule, respectively. When the surface of nanotube is exposed to light, oxygen at the surface yield superoxide radical $({}^{\circ}O_2^-)$. As a result of this, new energy levels in bandgaps are created, which helped in the degradation of dye molecule to carbon dioxide and water as illustrated in Fig. [7.3](#page-4-0) (Sadeghzadeh-Attar [2018](#page-15-7)). The photocatalytic mechanisms of dye removal using nanoparticles and nanotubes are discussed above, which showed light-dependent degradation of

Fig. 7.2 General mechanism of photodegradation of dye using nanoparticle

Fig. 7.3 General mechanism of photodegradation of dye using nanotube

dye. The degradation process involves excitation of electrons from valence band of nanomaterial leading to the formation of holes in valence band and their successful migration to conduction band. This helps in the enhancement of charge transfer process during the oxidation and reduction resulting in degradation of the dye molecule on nanomaterial surface.

7.4 Different Nanomaterials for Dye Removal

7.4.1 Nanoparticles

A variety of nanoparticles have been used as adsorbent for dye removal from industrial waste as summarized in Table [7.1.](#page-5-0) Being small in size, nanoparticles provide a large surface area, and they are highly pure with narrow size distribution and reproducible (Verma et al. 2019). In one of the studies, zinc oxide (ZnO) nanoparticles (NPs) were used as adsorbent to remove azo dye such as methyl orange (MO) and amaranth (AM) (Zafar et al. [2018](#page-16-1)). In another study, ZnO-NPs were used to adsorb three dyes: malachite green (MG), acid fuchsin (AF), and Congo red (CR) (Zhang et al. [2016\)](#page-16-2) and ZnO-NPs using alginate to adsorb methylene blue (MB) (Tamer et al. [2018](#page-15-9)). Acid Black 210 (AB 210) and Reactive Blue 19 (RB 19) dyes were adsorbed on 0.2 g of ZnO-NPs with adsorption capacities of 34.13 mg/g and 38.02 mg/g, respectively (Monsef Khoshhesab and Souhani [2018\)](#page-14-6). Reactive Blue 21 (RB 21) dye was also degraded via photodegradation using 50 mg of green-synthesized ZnO-NPs. In this study, it was also observed that RB 21 was fully decolorized in 270 min time. This shows that ZnO NPs are used as broad range nanoparticles for removal of a variety of dyes through adsorption. Other NPs such as copper nanoparticles (Davar et al. [2015](#page-13-10)) (CuNPs) have been used for catalytic

			Amount of	Adsorption/	
	Dyes	Method of	nanoparticle	reduction	
Nanoparticle	removed	removal	used	capacity	Reference
Zinc oxide nanoparticle	Methyl orange Amaranth	Adsorption	0.3 g	40 ppm	Zafar et al. (2018)
	Malachite green Acid Fuchsin Congo red	Adsorption	0.05 g	2963 mg/g 3307 mg/g 1554 mg/g	Zhang et al. (2016)
	Methylene blue	Adsorption	$0.025 - 0.3$ g	$33.87-$ 45.38%	Tamer et al. (2018)
	Acid black 210 Reactive blue 19	Adsorption	0.2 g	34.13 mg/g 38.02 mg/g	Monsef Khoshhesab and Souhani (2018)
	Reactive blue 21	Photodegradation	50 mg	NR	Davar et al. (2015)
Copper nanoparticles	Methylene blue Methyl red Congo red	Photocatalytic Degradation	$100 \mu M$	91.53% 73.89% 84.89%	Fathima et al. (2018)
Gold nanoparticles	Rhodamine B Methyl orange	Photocatalytic Degradation	5 _{mg}	87.64% 83.25%	Baruah et al. (2018)
	Congo red Methylene blue	Catalytic degradation	$50 \mu g/ml$	98% 88%	Nadaf and Kanase (2016)
Silica oxide nanoparticles	Methylene blue	Photocatalytic degradation	10 g/lt	85%	Aly and Abd-Elhamid (2018)
	Methylene blue	Adsorption	0.2 g	80.8 mg/g	Dhmees et al. (2018)
	Methylene blue	Adsorption	1000 mg/lt	679.9 mg/g	Peres et al. (2018)

Table 7.1 Summarizes the nanoparticles used in dye removal

degradation of MB, methyl red (MR), and CR. 100 μM of CuNPs were used for catalytic degradation of these three dyes (Fathima et al. [2018\)](#page-13-11). The photocatalytic degradation of Rhodamine B (RB) and MO had been achieved using gold nanoparticles (AuNPs). In this, 5 mg of each dye has been used for the process, which resulted in adsorption of 87.64% of RB and 83.25% of MO using AuNPs (Baruah et al. [2018](#page-12-3)). AuNPs were also biologically synthesized from *Bacillus marisfavi* and used for catalytic degradation of CR and MB. Ninety-eight percent of CR was degraded in 20 min, and 88% of MB was catalytically degraded in 10 min using AuNPs (Nadaf and Kanase [2016](#page-14-7)). The AuNPs are efficient in dye removal, but their synthesis is expensive, which fnally adds to the cost of dye removal. Silica oxide nanoparticles $(SiO₂-NPs)$ were used to degrade dye via photodegradation. This is possibly due to the presence of silanols, which can interact with dyes and make them chemically stable that can successfully degrade dye on silica surface. In a study, 10 g/l of the adsorbent is used, which decolorized MB to 85% within 90 s (Aly and Abd-Elhamid [2018](#page-12-4)). Adsorption of MB was also reported using silica nanoparticles (SiNPs) obtained from blast furnace in which 0.2 g of SiNPs as adsor-bent showed maximum sorption capacity of 80.8 mg/g (Dhmees et al. [2018](#page-13-12)). SiO_2 -NPs obtained from rice husk used for degradation of MB dye showed adsorption capacity of 679.9 mg/g with 80% dye removal using 1 g/l of the adsorbent (Peres et al. [2018\)](#page-14-8). Among all reported nanoparticles, ZnO NPs are best for the purpose of dye removal as they are easy to synthesize and are less costly as compared to the other nanoparticles. They also possess the inherent capacity to remove a broad range of toxic dyes from effuent.

7.4.2 Carbon Nanotubes

Carbon nanotubes (CNT) are allotropes of carbon, which achieve cylindrical shape during synthesis and are used for a variety of purposes. They are used for applications in optics and electronics and are one of the most important nanomaterials, which can be used to adsorb dyes present in wastewater effuent from various industries as summarized in Table [7.2.](#page-7-0) Here, we discuss some reported methods, which successfully used CNTs for dye removal. One of the methods exploits amorphous CNT for removal of two textile dyes, MO and RB. For this, two dye degradation methods were used: one was adsorption based, and the other was UV-based catalysis. In this method, concentration of dyes used was 4.79 mg/L and 3.27 mg/L for RB and MO, respectively. Though the concentration of adsorbent used was not reported, but it was stated that adsorbent took lesser time of 30 min to degrade MO as compared to 45 min for the RB dye. For both dyes, adsorbent had 90% removal efficiency (Dutta et al. [2018\)](#page-13-13). In some reported studies, composites were also used for dye removal process. A composite mixture of modifed CNT has been reported for removal of cationic dyes (MB, MG, RB) and anionic dye (MO). For achieving dye removal, multiwalled carbon nanotubes (MWCNT) were prepared and functionalized by acid treatment (ACNT), amine treatment ($NH₂CNT$), and finally with the heat treatment (HCNT). It was clear from the study that cationic dyes were adsorbed with high efficiency using ACNT and MWCNT, whereas the anionic dyes were decolorized using $NH₂CNT$. So, a composite of $ACNT/MH₂CNT$ and $MWCNT/$ NH2CNT was fnally used for dye removal (Dutta et al. [2017\)](#page-13-14). A nanohybrid of microporous carbon xerogels and MWCNT (CX/MWCNT) was successfully used for removal of RB dye in which concentration of adsorbent varied from 1 to 4 g/L. It was documented that nanohybrid prepared possessed dye removal efficiency ranging from 154 to 256 mg/g (Shouman and Fathy [2018\)](#page-15-10). MWCNTs were

Carbon nanotubes	Dyes removed	Method of removal	Amount of nanomaterial used	Adsorption/ reduction capacity	Reference
Amorphous CNT	Methyl orange Rhodamine B	Adsorption and UV-assisted catalysis	NR.	More than 90%	Dutta et al. (2018)
ACNT/ NH ₂ CNT MWCNT/ NH ₂ CNT	Methylene blue Malachite green Rhodamine B Methyl orange	Adsorption	5 mg ACNT/ MWCNT 5 mg NH2CNT Mixture	93% 91%	Dutta et al. (2017)
CX/ MWCNT	Rhodamine B	Adsorption	1 to 4 g/L	154-256 mg/g	Shouman and Fathy (2018)
MWCNTs/ Gly/β -CD	Methylene blue Acid blue 113 Methyl orange Disperse red 1	Adsorption	0.01 g	$90.90 \,\mathrm{mg/g}$ 172.41 mg/g 96.15 mg/g 500 mg/g	Mohammadi and Veisi (2018)
ZnO/ MWCNT	Congo red	Adsorption	9 _{mg}	99.8%	Seyed Arabi et al. (2019)

Table 7.2 Use of carbon nanotubes in dye removal

functionalized using β-cyclodextrin and glycine (Gly) for the adsorption of organic dyes such as MB, Acid Blue 113 (AB113), MO, and disperse red 1 (DR1). The 0.01 g of adsorbent (MWCNT/Gly/β-CD) was used for the dye removal (Mohammadi and Veisi [2018\)](#page-14-9). One work revealed that when ZnO-NPs were loaded on MWCNT, they successfully removed CR dye in the aqueous medium (Seyed Arabi et al. [2019\)](#page-15-11). So, it is clear from the above reported methods that CNTs work better when they are used as composite mixtures for dye removal.

7.4.3 Nanorods

Nanorods are one of the morphological structures of nanomaterials with size ranging from 1 to 100 nm and standard aspect ratio of 3–5. They can be easily synthesized from metal oxides and other semiconducting material through chemical synthesis. They have found a wide range applications in analytical methods and also used for adsorption of unused dyes. Different earlier reported methods have been documented in Table [7.3](#page-8-0) given below. Among one of these methods, manganite (γ-MnOOH)

Nanorods	Dyes removed	Method of removal	Amount of nanorod used	Adsorption/ reduction capacity/% dye removal	Reference
γ -MnOOH	Methylene blue	Adsorption	8 mg/L	89%	Varghese et al. (2017)
$AgCl-$ $NR-AC$	Methylene blue	Adsorption	15 mg	96%	Nekouei et al. (2016)
ZnCo ₂ O ₄	Methylene blue	Adsorption	5 mg	2400 mg/g	Lin et al. (2018)
$ZnO-$ $NR-AC$	Bromocresol green Eosin Y	Ultrasonic assisted adsorption	0.01 to 0.03 g	57.80 mg/g 61.73 mg/g	Ansari et al. (2016)
SBP	Methylene blue	Adsorption	0.05 g	1691.8 mg/g	Zhang et al. (2015)
ZnS/ $SnS/A-FA$	Congo red	Photocatalytic degradation	10 mg	NR	Kalpana and Selvaraj (2016)
WO ₃	Methylene blue	Adsorption	5.0 mg	57.6 mg/g	Park and Nam (2017)
Cu-doped- ZnO	Methyl Orange	Solar-assisted photodegradation	0.3 g/L	99%	Perillo and Atia (2018)
SnS nanorods	Tryphan blue	Photocatalytic degradation	0.9 mg/ml	More than 95%	Das and Dutta (2015)

Table 7.3 Nanorods used for dye degradation

nanorods were used as adsorbent for adsorption of MB dye. The concentration of adsorbent used was 8 mg/L, which successfully decolorized 89% of MB dye in aqueous solution (Varghese et al. [2017\)](#page-15-12). In one other method, AgCl nanorods were modifed on the activated carbon (AC) and AgCl-NR-AC composite when used in concentration of 15 mg successfully removed MB in aqueous solution and observed dye removal efficiency of about 96% in 16 min (Nekouei et al. [2016](#page-14-10)). $ZnCo₂O₄$ nanorods have also been used, which were synthesized through hydrothermal method and applied for dye removal. It was observed that 5 mg of nanorods when used as adsorbent removed MB dye with adsorption capacity of 2400 mg/g (Lin et al. [2018](#page-14-11)). An ultrasonic assisted adsorption of the Bromocresol Green (BCG) and Eosin Y (EY) dyes was also reported using ZnO nanorods and AC complex. The adsorption capacities recorded were 57.80 mg/g and 61.73 mg/g for BCG and EY, respectively, when 0.01–0.03 g of adsorbent was used (Ansari et al. [2016\)](#page-12-5). In this, 0.05 g of strontium phosphate and barium phosphate (SBP) composite of nanorod had been used for MB dye removal with adsorption capacity of 1691.8 mg/g (Zhang et al. [2015](#page-16-3)). Zinc sulfde (ZnS) in combination with tin sulfde (SnS) was used to synthesize ZnS/SnS/A-FA nanorods for removal of CR dye from wastewater. The nanorods were in concentration of 10 mg for removal of dye in the wastewater. The dye was completely photodegraded in 150 min (Kalpana and Selvaraj [2016\)](#page-13-15). Other methods for dye removal using nanorods are also available using tungsten

trioxide (WO_3) (Park and Nam [2017](#page-14-12)), copper (Cu)-doped-ZnO (Perillo and Atia [2018\)](#page-15-13), SnS nanorods (Das and Dutta [2015](#page-13-16)), etc. All the above-reported methods demonstrated that nanorods are more effcient in dye removal when they are used in combination with materials, which enhances their dye removal capacity.

7.4.4 Graphene

Graphene is an allotropic form of carbon in which carbon atoms are arranged in single-layer hexagonal lattice. Its basic structure reveals that there is a small overlap between valence band and conduction band, which makes it an important nanomaterial for dye removal. Many researchers have used graphene for dye removal as summarized in Table [7.4.](#page-10-0) A composite of 3D graphene and calcium carbonate $(CaCO₃)$ was synthesized in the presence of calcium carbonate and iron oxide nanoparticles. Further, this nanocomposite of graphene was used for the removal of Acid Red 88 (AR88) dye. The amount of adsorbent used was 87 mg to remove 100% of AR88 in 18 min (Arsalani et al. [2018](#page-12-6)). Three-dimensional graphene was functionalized with magnetic citric acid to prepare a nanocomposite (MCF3DG) for removal of crystal violet (CV) in aqueous medium (Nasiri and Arsalani [2018\)](#page-14-13). Reduced graphene oxide (rGO) coupled with bismuth vanadate $(BiVO₄)$ was used to remove MG and RB dye. It was reported that the adsorbent used possessed low catalytic and dye removal effciency. MG was degraded to 99.5% in two hours, and RB was decolorized 99.84% in four hours (Zhang et al. [2018](#page-16-4)). Several other methods are also available, which include liquid laser-treated rGO (Russo et al. [2015\)](#page-15-14), polyvinyl alcohol (PVA) hydrogel in combination with GO (Li et al. [2014\)](#page-14-14), magnetic sulfonic and graphene nanocomposite $G-SO₃H/Fe₃O₄$ (Wang et al. [2013\)](#page-16-5), GO nanosheet functionalized using dithiocarbamate (GO-DTC) (Mahmoodi et al. [2017\)](#page-14-15), GO and cellulose nanowhisker hydrogel nanocomposite removed MO and RB dye in 20 min (Soleimani et al. [2018](#page-15-15)), rGO and $TiO₂$ nanocomposite (TiO₂[@]) rGO) (Ali et al. [2018](#page-12-7)), GO and chitosan aerogel composite (GOCA) (Lai et al. [2019\)](#page-13-17), magnetite nanoparticles and GO nanocomposite $(Fe_3O_4@GO)$ (Mishra [2018\)](#page-14-16), graphene-tannic acid hydrogel (GT hydrogel) (Tang et al. [2018](#page-15-16)), sulfonated GO (SGO) (Wei et al. [2018](#page-16-6)), and GO and magnetic iron oxide NPs (GO-MNP) (Othman et al. [2018\)](#page-14-17).

7.4.5 Fullerene

Fullerene is also an allotrope of carbon, which is hollow sphere in shape. They are also known as buckminsterfullerene or the bulkyball. Fullerene is also used for dye removal, and the reported methods are summarized in Table [7.5.](#page-11-0) Fullerene (C_{60}) has been used as composite with $TiO₂$ for removal of CV dye. The dye-removing capacity of 82% was achieved when $TiO₂$ and $C₆₀$ fullerene nanocomposites were used in

Graphene	Dyes removed	Method of removal	Amount of graphene used	Adsorption/ reduction capacity/% dye removal	Reference
3D graphene aerogel/CaCO ₃	Acid red 88	Adsorption	87 mg	100%	Arsalani et al. (2018)
MCF3DG	Crystal violet	Adsorption	28 mg	100%	Nasiri and Arsalani (2018)
$BiVO4-rGO$	Malachite green Rhodamine B	Adsorption enhanced with visible light irradiation	50 mg	99.5% 99.84%	Zhang et al. (2018)
rGO	Methylene blue	Adsorption	0.17 mg/ml	746 mg/g	Russo et al. (2015)
PVA/GO hydrogels	Methylene blue	Adsorption	1 _g	NR	Li et al. (2014)
$G-SO3H/Fe3O4$	Safranine T Neutral red Victoria blue	Adsorption	10 mg	199.3 mg/g 216.8 mg/g 200.6 mg/g	Wang et al. (2013)
GO-DTC	Basic blue 41 Basic red 46	Adsorption	$0.01 - 0.04$ g	128.5 mg/g 111 mg/g	Mahmoodi et al. (2017)
GO-cellulose nanowhisker hydrogel	Methylene blue Rhodamine B	Adsorption	0.025 g	100% 90%	Soleimani et al. (2018)
TiO ₂ @rGO	Rhodamine B	Photodegradation	$0.1 - 0.5$ g	97%	Ali et al. (2018)
GOCA	Metanil yellow	Adsorption	8 _{mg}	430.99 mg/g	Lai et al. (2019)
Fe ₃ O ₄ @GO	Rhodamine 6G	Adsorption	$0.005 -$ 0.02 g	68-89%	Mishra (2018)
GT hydrogel	Methylene blue	Adsorption	NR	714 mg/g	Tang et al. (2018)
SGO	Methylene blue	Adsorption	1 mg/25 ml	2530 mg/g	Wei et al. (2018)
GO-MNP	Methylene blue	Adsorption	$10 - 15$ mg	98%	Othman et al. (2018)

Table 7.4 Graphene sheets used in dye removal

10 mg concentration (Panahian et al. 2018). Fullerene-modified SiO₂ material was used for efficient removal of MB dye. The percentage of dye removed via photodegradation was 45% and 90% under VIS and UVC light, respectively (Rogozea et al. [2015\)](#page-15-17). One of the studies was also reported in which $Fe₂O₃$ was doped on $C₆₀$ to achieve a composite of C_{60} -Fe₂O₃. The composite was further used for

Fullerene	Dyes removed	Method of removal	Amount of fullerene used	Adsorption/ reduction capacity/% dye removal	Reference
$F-TiO2(B)$ / fullerene	Crystal violet	Photocatalysis	10 mg	82%	Panahian et al. (2018)
Fullerene- modified silica	Methylene blue	Photodegradation	20 mg	45% via VIS 90% via UVC	Rogozea et al. (2015)
C_{60} -Fe ₂ O ₃	Methylene blue Rhodamine B Methyl orange	Photodegradation	50 mg/L	98.9%	Zou et al. (2018)

Table 7.5 Fullerene structures for dye removal

photocatalytic degradation of three dyes MB, RhB, and MO in the presence of hydrogen peroxide. 98.9% dye decolorization was achieved in 80 min (Zou et al. [2018\)](#page-16-7). The fullerene structures are less exploited as compared to other nanomaterials. This may be due to complexity in their structure,and they are not easy to synthesize.

7.5 Conclusion and Future Prospects

Untreated industrial discharge contains toxic dye, and they are being released in open environment, which is extensively harmful to living beings and environment. Variety of conventional methods is available for effuent treatment, but these methods suffer from limitations of less effciency, costly, labor-intensive, and timeconsuming. Therefore, the use of nanomaterials for dye degradation is considered as novel and eco-friendly approach. Many types of nanomaterials are being reported for dye removal such as nanoparticles, nanotubes, nanorods, graphene, and fullerene. Nanomaterials possess unique properties like highly electroactive, small size, high surface area, easy to synthesize in laboratory, nontoxic nature, biodegradability, and biocompatibility, which make them suitable for dye removal. Due to these properties, nanomaterials can be used with other composites as reported in this review. It is suggested that photocatalytic degradation of dyes is based on light irradiation, which helps in excitation of electrons and causes movement of electron to form electron hole pair, and formation of radicals takes place, which caused degradation of dyes. Out of nanomaterials, which are discussed here, nanoparticles are more exploited. Although the researcher has used a variety of nanomaterials, but fullerene is less exploited. Fullerene should be used as nonabsorbent in combination with the other nanomaterials. Quantum dots are also to be explored for their ability to adsorb dye from the effuent. Besides this toxicity of nanomaterials used as nanosorbents in dye removal must be examined. There are also some challenges in using nanomaterials for dye degradation such as photocatalyst loading, dye concentration, pH of the medium, intensity of light, temperature, photocatalyst morphology, wavelength of light used in photodegradation, effect of oxidizing species, and so on. These above parameters should be optimized carefully before using any nanomaterial for photodegradation of harmful dye.

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Questions

- 1. Write a note on classifcation of dyes.
- 2. What are the toxic effects of dyes on the environment and living beings?
- 3. Discuss in detail conventional methods used to remove dyes.
- 4. Write down different types of nanomaterials along with their properties.
- 5. How nanomaterials can be used for removal of dyes and what are their inherent properties, which make them an excellent candidate for dye removal?
- 6. Discuss the mechanism dye removal via photodegradation.

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