

# Degradation of hazardous organic dyes in water by nanomaterials

Uma Shanker<sup>1</sup>  · Manviri Rani<sup>1</sup> · Vidhisha Jassal<sup>1</sup>

Received: 22 December 2016 / Accepted: 12 June 2017 / Published online: 21 June 2017  
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**Abstract** There is about 700,000 tonnes of dyes, of more than 10,000 types, that are used as coloring agents in industries, mainly for textile. The release of dyes in natural media is of concern due to their high persistence, toxicity and potential to bioaccumulate in living organisms. In particular, the most commercialized and carcinogenic azo dyes, that possess a benzidine function, needs urgent attention. Here, we review the current status of cationic and anionic dyes. We present dye removal techniques using nanoparticles through adsorption and degradation. Among dye removal techniques, adsorption was found the most efficient and cheap. For that, conventional adsorbents such as commercial activated carbon, chitosan and natural waste are often employed. We discuss the use of ZnO, TiO<sub>2</sub> and Fe<sup>0</sup> to remove dye pollution.

**Keywords** Hazardous dyes · Nanomaterials · Adsorption · Photocatalysts · Degradation

## Introduction

With the growing pace of industrialization, the discharge of effluents containing dyes, pesticides, phenols and other persistent organic pollutants is increasing at a rapid rate. They are posing severe threats to the living organisms due to their harmful and toxic effects (Natarajan et al. 2011; Gupta et al. 2012c; Rani, 2012). Sometimes, their

metabolites are even more toxic than the parent compounds (Tian et al. 2009; Gupta et al. 2011, 2012a, b; Rani et al. 2017a, b). Until 1850, all important colors were used to achieve with the help of natural dyes. After the Perkin's discovery, the development of commercial colorants was so fast that within 50 years, more than 90% of the synthetic dyes were used (Gordon and Gregory 1983). Within few decades, the natural dye industries in Europe collapsed and market was crowded with the synthetic ones. At present, a statistics according to the Color Index states that there are approximately 10,000 types of dyes being manufactured with their annual production of more than 700,000 tonnes (Moussavi and Mahmoudi 2009). The reasons behind the success and the widespread use of these synthetic dyes lie in their superior tinctorial strength, economical, easy availability of raw materials, easy preparation, good fastness properties and ability to cover the whole shade range. Among all the known commercial dyes, azo dyes are the most used. Other classes of dye include phthalocyanine, anthraquinone, polymethines and aryl-carboniums (Gregory 1990). China is the world's biggest producer and suppliers of organic color pigments because of rapid industrialization. However, production in Europe, USA and Japan reduced in the last years due to plant shutdowns and restructurings. This is an issue of health concern to living beings because of greater exposure of these organic pigments (Fig. 1) (Chemical Economics Handbook 2015). The total production (in thousand MT) of various dyes in India from 2010–2015 as per report of Ministry of Chemical and Fertilizers, Department of Chemicals and Petrochemicals, Govt. of India (Ministry of Chemical and Fertilizers, India (MCF, India) 2016) is shown in Table 1.

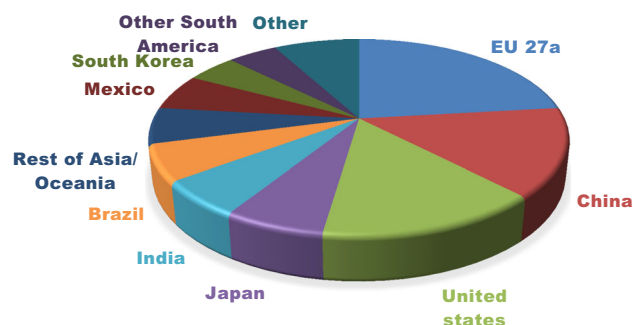
Dyes are highly toxic and pose the strong tendency toward eutrophication (Prevot et al. 2001). During the last few decades, water and soil pollution problems have

✉ Uma Shanker  
shankeru@nitj.ac.in; umaorganic29@gmail.com

<sup>1</sup> Office Number-CE-306, Department of Chemistry,  
Dr B R Ambedkar National Institute of Technology,  
Jalandhar, Punjab 144011, India

become major issues of concern across the globe. Main source is the extensive use of harmful dyes and dyestuffs in various sectors such as textile, cosmetics, paper, food processing and drug industries (Sahoo et al. 2005). The untreated discharged dyes (around 10%) impart an intense color even at a low concentration (less than 1 ppm), thereby making the water highly detrimental (Bazin et al. 2012; Zhang and Wu 2014). The dissolved oxygen level gets reduced because the molecules of dyes prevent sunlight to the bulk of water system. The contaminated water also has an increased biological oxygen demand (Carmen and Daniela 2012). As a consequence, these exert an enormous environmental hazard to the biota (Mohan et al. 2002; William et al. 2008; Safavi and Momeni 2012). Several synthetic dyes, particularly the azo dyes, are highly carcinogenic and need an immediate attention (Ratna 2012).

In order to reduce the acute diverse effects of dyes, different strategies like in depth study of dye constituents and their metabolites have been developed (Chung et al. 1981; Holme 1984). These dyes are resistant to degradation because of their high stability toward heat, light and oxidizing agents (Jain and Sikarwar 2008). Precisely



**Fig. 1** Worldwide consumption (2014) of organic color pigments (Published in October 2015) (Chemical Economics Handbook 2015)

discussing about the azo dyes, they produced aromatic amines which are highly carcinogenic and even an explosive. They also contain the most common carcinogen, i.e., benzidine, which must be treated effectively before discharging into the environment (San et al. 2014). The azo ( $-N=N-$ ) group in cooperation with substituted aromatic groups imparts high brightness to the azo dyes (Bhatnagar and Jain 2005).

## Dye removal techniques

Increasing population, fast pace of industrialization, modernization of civilizations, agricultural as well as domestic wastes and several environmental changes are declining the quality of water. Hence, there is a need to eradicate this problem completely (Nemerow and Dasgupta 1991; Tchobanoglous and Franklin 1991; Ali and Aboul-Enein 2004). Several disadvantages of using dyes such as generation of large amount of secondary waste as well as sludge, toxicity and persistence encouraged to design and develop the efficient removal methods (Tan et al. 2008; Sachdeva and Kumar 2009; Zonoozi et al. 2009; Ghaedi et al. 2011). In the last few years, several physical (adsorption, coagulation-flocculation, membrane filtration chemical (ion-exchange method, chemical precipitation, oxidation, catalytic degradation) as well as biological methods (microbial degradation) have been developed to treat toxic dyes from wastewater reservoirs (Galindo et al. 2001; Kuo and Ho 2001).

Among all, adsorption was found as the most efficient technique because of its simplicity and economical approach (Kyzas et al. 2012; Kumar et al. 2014; Ghaedi et al. 2015; Sheibani et al. 2015). Dyes molecules get adsorbed on the surface of an adsorbent through hydrogen bonding, van der Waals interactions or hydrophobic forces (Gupta and Suhas 2009; Kumar et al. 2014). The initial dye

**Table 1** Total production of various dyes for the year 2010–2015 in India (Annual Report 2015–2016)

Class of dyes	2010–2011	2011–2012	2012–2013	2013–2014	2014–2015
Azo dyes	13.96	12.10	12.72	13.46	10.59
Disperse dyes	28.72	29.44	28.26	29.21	29.56
Fast color bases	0.09	0.04	0.02	0.01	0.01
Ingrain dyes	0.69	0.98	0.58	0.51	0.44
Optical whitening agents	15.02	14.14	18.17	23.74	22.94
Organic pigment colors	56.35	51.77	44.46	68.67	76.89
Pigment emulsions	5.89	5.22	6.48	7.34	9.64
Reactive dyes	76.88	83.38	87.60	95.42	89.47
Sulfur dyes (sulfur black)	8.58	7.02	6.58	7.57	9.38
Vat dyes	1.94	1.69	1.38	1.60	1.77
Solubilized vat dyes	0.04	0.03	0.03	0.02	0.03
Naphthols	0.07	0.04	0.00	0.00	0.00

concentration, pH of the solution, temperature, contact time, dosage of adsorbent, size of adsorbent and interaction affinity between particles are the main factors governing the performance of most of the adsorption processes. Having high surface-to-volume ratio, nanomaterials (organic and inorganic) showed superior properties and considered to be the future building blocks of advanced devices in various interdisciplinary fields (Baioni et al. 2007; Dierick et al. 2008; Kleinstreuer et al. 2008; Garg et al. 2011; Lattuada and Hatton 2011). The pursuit for smart materials with innovative technology and much improved efficiency has led to extensive research in this field (Buzea et al. 2007; Jassal et al. 2015a, b; Shanker et al. 2016a, b).

Because of high porosity and large surface area ( $500\text{--}2000\text{ m}^2\text{ g}^{-1}$ ), commercial activated carbon has been widely used by dye manufacturing factories for dye removal (Carrott et al. 1991; Abdullah et al. 2009). However, the high production and operation cost of AC and very low surface area of commercial chitosan (Crini and Badot 2008) have motivated the search for alternative adsorbents such as nanomaterials that are both economical and efficient due to unique features. In the current scenario, researchers have synthesized a wide variety of nanomaterials like Zn, Mg and Ti (Raliya and Tarafdar 2014), ZnS (Naskar et al. 2006), metal oxides (Shanker et al. 2016a, b), nanochitosan (Kocak et al. 2012), graphene oxide (Jiang et al. 2016) via ecofriendly methods. Gold nanoparticles (4–15 nm) in aqueous solution and carbon nanotube were developed by microwave-assisted (Bayazit et al. 2016) and coal pyrolysis (Moothi et al. 2015), respectively. Jassal et al. (2015a, b) have developed metal hexacyanoferrates nanoparticles of different size and shape and applied them as nanocatalyst in dye degradation (Jassal et al. 2016a) and oxidation of aromatic amine (Jassal et al. 2015a, b, 2016c). Keeping these points into consideration, these nanomaterials can be used on a commercial scale, though this needs further exploration. Commercialization of nanomaterials can greatly help in solving the real-world wastewater problems caused due to hazardous dyes.

Overall, nanomaterials act as excellent adsorbents because of advantages of possessing the large specific surface area, small diffusion resistance, higher adsorption capacity, and faster adsorption equilibrium (Ma et al. 2011). Moreover, magnetic nanoparticles are also widely used due to their easy separation by applying an external magnetic field (Kong et al. 2012; Xu et al. 2013a). These features have attracted many researchers worldwide, which contributed to advancements in the removal of dyes from wastewater. Literature search on SciFinder depicted that there is a sharp increase in the removal of dyestuffs from wastewater using nanoadsorbents. Table 2 describes the list of different nanomaterials employed for removing

various dyes. Therefore, it is considered worthwhile to write this review in order to summarize and address the advancements in use of nanomaterials for the removal of dyes.

## Anionic dyes

### Methyl orange

Methyl orange comes under anionic category of synthetic dyes and causes several health problems (Chen et al. 2010). Application of this dye as a weak acid base indicator has contributed to its increased utility in printing, paper manufacturing, textile, pharmaceuticals and food industries (Mittal et al. 2007). Various reports regarding the photocatalytic degradation of MO dye using nanomaterials have been available. For example, Lee et al. (2015) used Al-doped ZnO nanoparticles (3% of Al) photocatalyst for 95% of degradation within 120 min. Maximum degradation of methyl orange can also be achieved using silver nanoparticles within 12 h (Kumar et al. 2013). Lead oxide nanoparticles loaded with activated carbon were found potential at optimized parameters of 22 min, pH  $\sim$  2 and 0.02 g catalyst dosage (Ghaedi et al. 2016). Kaur and Singhal (2014a, b) used ZnO and transition metal-doped ZnO nanoparticles and identified 11 intermediates during the degradation process. Combined effect of UV light and ZnO nanoparticles greatly enhanced the degradation of methyl orange (complete degradation in 40 min) (Fig. 2) (Kumar et al. 2015). Thapa et al. (2012) used TiO<sub>2</sub> nanoparticles under UV light for degrading 98% of the dye. Hamadani et al. (2014) observed that photodegradation of methyl orange was greatly enhanced by using 5% molar solution of Cr<sup>3+</sup>-doped TiO<sub>2</sub> nanoparticles.

Cr<sup>3+</sup> on the surface of TiO<sub>2</sub> can trap photogenerated e<sup>−</sup>, thus reducing recombination of e<sup>−</sup> and h<sup>+</sup> pairs, and enhance the photocatalytic activity of TiO<sub>2</sub> under visible light irradiation (Li et al. 2013).

### Congo red

Congo red is an anionic dye and widely used in printing, plastic, leather, paper and textile industries. It can also be used as a histological stain and pH indicator for amyloid in the diagnosis of amyloidosis as well as for detecting the free hydrochloric acid in gastric contents (Shu et al. 2015). Because of non-biodegradable nature, it causes visual spolioation to the water and the landmass (Debnath et al. 2015).

Several studies were carried out for removing Congo red successfully using different nanomaterials, such as

**Table 2** List of various anionic and cationic dyes degraded using different nanoparticles

S.No.	Nanoparticles	Dyes removed	Remarks	References
1.	Nanocrystalline TiO <sub>2</sub> /activated carbon composite	Chromotrope 2R	UV irradiation of the dye solution resulted in its effective degradation with initial quantum yield of 1.01% using 80-AC-TiO <sub>2</sub> calcined at 450 °C	Wang et al. (2007)
2.	Si <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)/Fe <sub>3</sub> O <sub>4</sub>	Congo red	High adsorption capacity of approximately 89% was achieved using 0.20 g of the catalyst	Zhang et al. (2016)
3.	Fe/Ni bimetallic nanoparticles supported on polyacrylic acid-functionalized commercial polyvinylidene fluoride (PVDF) membrane	Methyl orange	More than 80% of the dye degradation was observed within 120 min at pH 4.0 due to the formation of nickel hydride which facilitated azo dye adsorption process	Sikhwivhilu and Moutloali (2015)
4.	Intercalated CdS nanoparticles into titanate	Congo Red	In almost 15 min, colorless time is reached, i.e., color of the solution was removed completely using 0.08 g of the catalyst	Sehati and Entezari (2016)
5.	Silver-TiO <sub>2</sub> nanocomposites	Eosin Y	100% of the dye was degraded within 160 min with 50% of mineralization	Alfaro et al. (2011)
6.	NiO nanoparticles	Fluorescein	Degradation of the dye was carried out under sunlight, UV and CFL irradiation. A higher photocatalytic activity of 60% was observed under sunlight in 1 h, followed by CFL irradiation	Raj et al. (2016)
7.	Multielements-doped ZrO <sub>2</sub> nanoparticles	Indigo carmine	In a time period of 150 min, complete photodegradation of the dye was achieved Catalyst: Eu,C,N,S-doped ZrO <sub>2</sub> (0.6% Eu)	Agorku et al. (2015)
8.	Cr-doped titanium oxide nanoparticles	Methyl orange	Nearly 90% of the dye was degraded using 5% mol Cr <sup>3+</sup> -doped TiO <sub>2</sub> nanoparticles in a time period of around 350 min	Hamadian et al. (2014)
9.	Bimetallic Fe/Pd nanoparticles	Orange II	A high degradation of 98% was reported using green synthesized bimetallic nanoparticles, whereas only 16% of the dye was degraded using Fe nanoparticles	Luo et al. (2016)
10.	SnO <sub>2</sub> nanoflowers	Rose Bengal	Within 90 min, ~ 96% of the dye was degraded successfully	Malik et al. (2015)
11.	ZnO nanoparticles	Eriochrome Black T	Enhanced photocatalytic degradation of 88% was achieved under basic conditions (pH 11.0) due to higher concentration of hydroxyl radicals. At pH 4.0 and 8.0, ~ 75% and 83% of the dye were degraded, respectively	Kazeminezhad and Sadollahkhani (2014)
12.	Au nanoparticles loaded on activated carbon	Alizarin red S	In a short time of 5 min, > 95% of the dye was degraded using 0.015 g of the adsorbent	Roosta et al. (2014)
13.	Cu <sub>0.5</sub> Mn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub> nanoparticles	Brilliant green	Under optimized conditions, 92% adsorption efficiency was observed for Mn <sub>0.5</sub> Cu <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub> . The adsorption behavior of nanoparticles followed the order: MnFe <sub>2</sub> O <sub>4</sub> < CuFe <sub>2</sub> O <sub>4</sub> < Mn <sub>0.2</sub> Cu <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub> < Mn <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub> < Mn <sub>0.4</sub> Cu <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub> < Mn <sub>0.5</sub> Cu <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub>	Hashemian et al. (2015)
14.	CuO nanoparticles	Coomassie Brilliant Blue-R-250	CuO nanoparticles synthesized using <i>Carica papaya</i> leaves extract led to a substantial decrease in the intensity of dye (~ 43.75% degradation in 90 min)	Sankar et al. (2014)
15.	Nanocrystalline CoFe <sub>2</sub> O <sub>4</sub>	Brilliant Blue-R	65–93% of the dye was adsorbed within 1 min which attained equilibrium in 60–120 min	Khan et al. (2015)
16.	Graphene quantum dots	New Fuchsin	At dye concentration of 6 ppm, 95.83% degradation was obtained within 110 min	Roushani et al. (2015)

**Table 2** continued

S.No.	Nanoparticles	Dyes removed	Remarks	References
17.	CdS nanoparticles embedded on zeolite A	Crystal violet	Utilizing sunlight as the radiation source 80% photodecolorization was obtained in about 20 min	Nezamzadeh-Ejhi and Banan (2012)
18.	MnO <sub>2</sub> nanosheets	Malachite green	In 120 min, ~99% decolorization of dye was achieved with 0.5 g L <sup>-1</sup> and 50 mg L <sup>-1</sup> dose of catalyst and dye concentration, respectively	Saha and Pal (2014)
19.	Nanographite/Fe <sub>3</sub> O <sub>4</sub> composite	Methyl violet	Adsorption of the dye strongly increased with increasing pH, particularly above 10.0(98.9%) because with the rising pH negative charges are increased which favors the interaction between cationic dye and negatively charged adsorbent	Li et al. (2014)
20.	Ta-doped ZnO nanoparticles	Methylene blue	At pH 8.0, maximum degradation (~99%) was achieved using 1% Ta-doped ZnO catalyst annealed at 700 °C because at low alkaline pH high hydroxylation of the catalyst surface takes place which attracts the cationic dye	Kong et al. (2010)
21.	ZnO nanopowder	Rhodamine B	In a time of around 8 min, >95% of the dye was successfully degraded under solar light irradiation and basic pH	Nagaraja et al. (2012)
22.	Cuprous iodide-cupric oxide nanocomposite	Malachite green	High adsorption capacity around 136.6 mg g <sup>-1</sup> of the catalyst was observed for the rapid removal of dye in a time less than 20 min	Nekouei et al. (2016)

magnetic Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)/Fe<sub>3</sub>O<sub>4</sub> nanorods (Zhang et al. 2016), sulfanilic acid-modified P25 TiO<sub>2</sub> nanoparticles (Guo et al. 2012) and bimetallic Fe–Zn nanoparticles (Gautam et al. 2015). Metallic nanoparticles like Ru act as electron mediator in transfer of electron from reducing agent to azo bond, and hence, the rate of degradation of Congo red was found to be increased by a factor of two hundred (Fig. 3) (Gupta et al. 2013a). The adsorption or removal ability of undoped cobalt ferrite nanoparticles for Congo red was 131 mg g<sup>-1</sup> (Zhao et al. 2014) which further improved to 161 mg g<sup>-1</sup> with Gd<sup>3+</sup>-doped cobalt ferrites (CoFe<sub>2-x</sub>Gd<sub>x</sub>O<sub>4</sub>). *Amaranthus gangeticus* Linn (Chinese spinach) leaf extract was used to synthesize silver nanoparticles which exhibited good catalytic efficiency (more than 50% within 15 min) for degrading Congo red dye (Kolya et al. 2015).

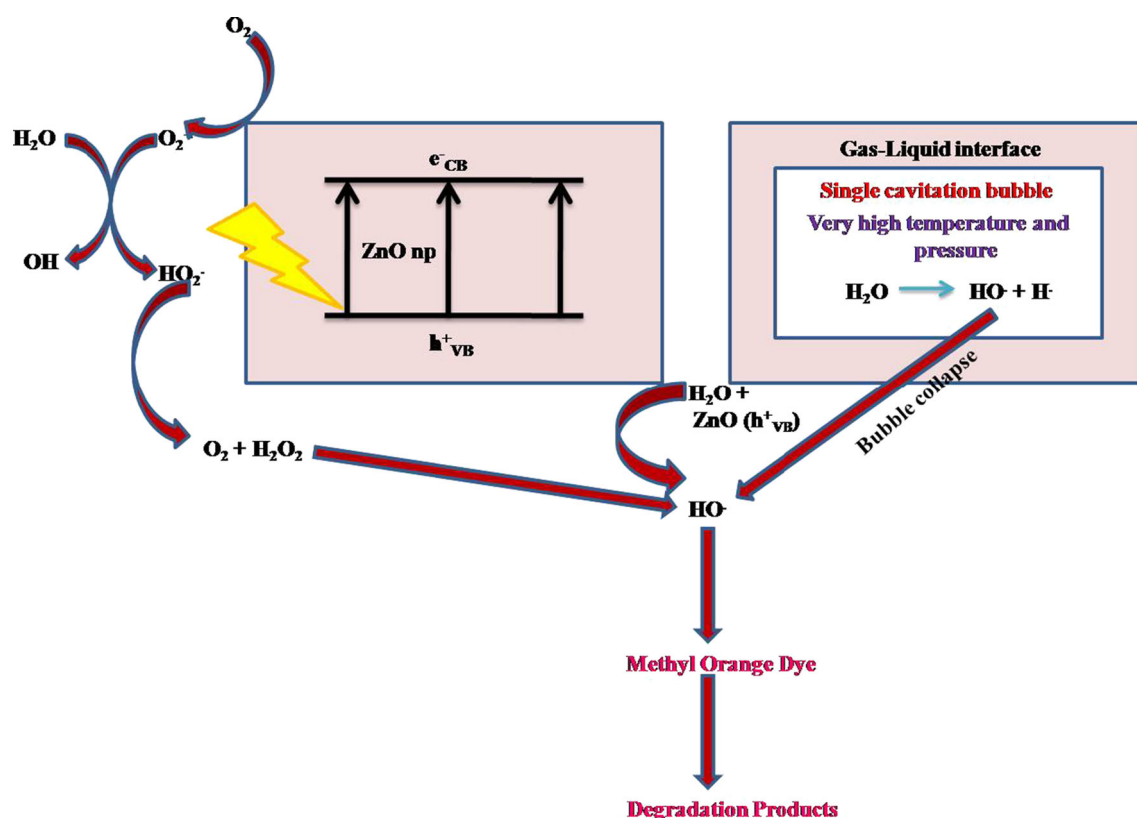
### Alizarin red S

Alizarin red S is an anthraquinone dye with carcinogenic characteristic and widely used in textile industries. Alizarin red S is resistant to degradation because of its complex aromatic structure, high thermal, optical, and physico-chemical stability. Therefore, an effective catalyst is required for the degradation of this dye (Moriguchi et al. 2003; Prillo et al. 2009; Kurepa et al. 2010; Gautam et al. 2013).

Alizarin red S was successfully degraded (77% in 90 min) under UV light irradiation by ZnO nanoparticles. The generation of electron–hole pair on the surface of nanoparticles enhances their photocatalytic activity (Kansal et al. 2013a). Polypyrrole-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles with an amount of 0.1–0.12 g/100 mL at pH 4.0–5.4 gave maximum degradation of Alizarin red S in 1 h (Gholivand et al. 2015). Bismuth vanadate (BiVO<sub>4</sub>) nanocrystals and gold nanoparticles loaded on activated carbon were employed as a photocatalyst to successfully degrading the 99.6% (180 min) and 95% (5 min) of the dye, respectively (Abraham et al. 2016; Roosta et al. 2014). Interestingly, degradation of Alizarin red S was carried out more effectively in microwave oven than in a photochemical reactor using ZnO/poly (1-naphthylamine) nanohybrids due to higher extent of ·OH radical generation. Several degradation fragments were analyzed by liquid chromatography–mass spectrometer technique (Riaz et al. 2016), as shown in Fig. 4.

### Eosin Y

Eosin Y is brominated anionic heterocyclic dye and widely used in routine staining of histological tissue sections such as epithelial cells, collagen and erythrocytes (Fischer and



**Fig. 2** Photocatalytic and sonocatalytic degradation of methyl orange using ZnO nanoparticles (Kumar et al. 2015)

Jacobson 2006). It is also used in the fields of printing, dyeing, pigment, leather and fluorescent. The release of eosin Y into water can cause serious environmental problem due to its dark color and toxicity (Culling et al. 1985; Lewis 1992; Lunn and Sansone 1994; Muruganandham and Swaminathan 2004).

Photodegradation studies using different nanomaterials for the effective removal of eosin Y are reported (Alfaro et al. 2011; Liu et al. 2014; Vignesh et al. 2012; Ramanan et al. 2014; Bhattacharjee and Ahmaruzzaman 2015). Two-dimensional CuO nanoleaves and silver–TiO<sub>2</sub> nanocomposites could successfully degrade (100%) the dye within 45 min and 160 min, respectively (Alfaro et al. 2011; Liu et al. 2014). Hes-TiO<sub>2</sub> (Hesperidin modified TiO<sub>2</sub>) nanoparticles also showed high catalytic efficiency (96%) in acidic pH (4.0) and irradiation time of 180 min. Dye exists in its anionic form in aqueous solution and acidic pH favors the adsorption process. Possible photodegradation products of eosin Y (Vignesh et al. 2012) are shown in Fig. 5. Liu et al. (2014) found that TiO<sub>2</sub>/N-graphene nanocomposite (5 wt %) was effective in degrading the dye due to maximum surface contact between TiO<sub>2</sub> and dye. Photodegradation ratio of 63.4% was achieved after 3 h of visible light irradiation.

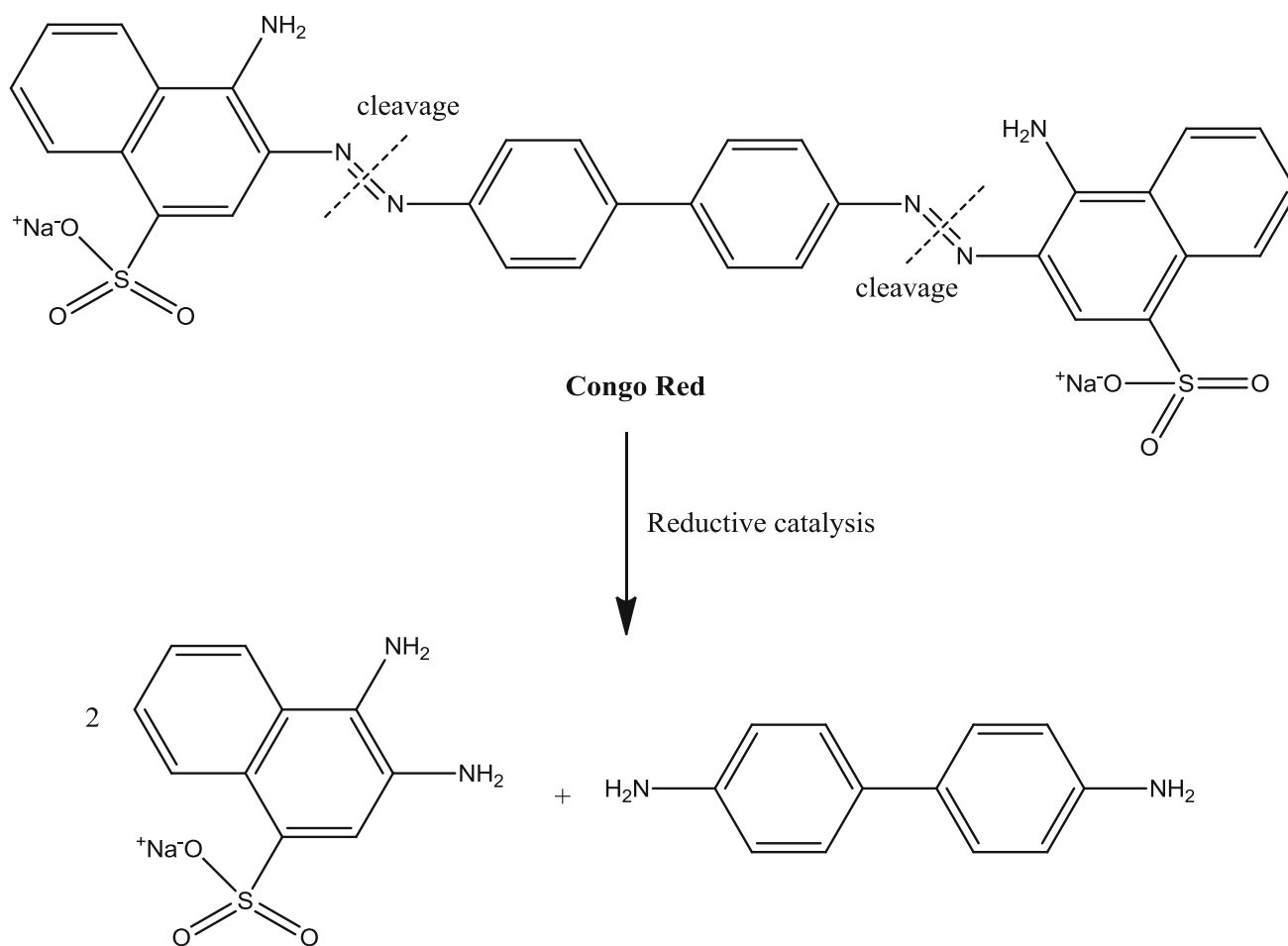
## Orange II

Orange II is an azo dye and widely used in industries such as rubber, textiles and leather. These are known to be more toxic and carcinogenic because of the low reactivity of azo bond (Nam and Tratnyek 2000; Kousha et al. 2012).

TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and bimetallic Fe/Pd nanoparticles were employed for the successful degradation of Orange II (Thapa et al. 2012; Chen et al. 2014; Luo et al. 2016). Fe<sub>3</sub>O<sub>4</sub> nanoparticles removed 99.6% of the dye at pH of 2.7 and 42 °C temperature (Chen et al. 2014), whereas 98% (12 h) and 99% (20 min) of the dye was degraded using bimetallic Fe/Pd and TiO<sub>2</sub> nanoparticles, respectively (Luo et al. 2016; Thapa et al. 2012). A conceptual mechanism for the degradation of dye using bimetallic Fe/Pd nanoparticles has been proposed (Luo et al. 2016) by the authors and is shown in Fig. 6.

## Rose Bengal

Rose Bengal is an important xanthene dye which is characterized by the presence of xanthene nucleus with aromatic groups as chromophore. It is widely used in printing,



**Fig. 3** Reductive cleavage of azo bonds of congo red using metallic nanoparticles (Gupta et al. 2013a)

dyeing, photochemical and textile industries. Xanthene dyes are reported to be cytotoxic, cytostatic, genotoxic and mutagenic (Chequer et al. 2012; Ritchie et al. 2013).

Several photocatalysts have been used so far for removing Rose Bengal successfully. Hexagonal  $\gamma$ - $\text{Fe}_2\text{O}_3$  nanoparticles effectively degraded the dye in visible light (Dutta et al. 2014). Using ZnO nanoparticles, approximately 98% degradation of the dye was achieved within 90 min (Kaur and Singhal 2014a, b). Porous 3-D hierarchical  $\text{SnO}_2$  nanoflowers also degraded the dye within 90 min (96% degradation) (Malik et al. 2015).

### Eriochrome Black T

Eriochrome Black T is used in dyeing nylon, multifibers, silk and wool as well as in laboratories for estimation of  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions (Jo and Dasgupta 2003). Eriochrome Black T is carcinogenic azo dye with its intermediate product naphthaquinone (San et al. 2014). Therefore, it is always a serious matter around the globe

for effective treatment of wastewater containing Eriochrome Black T (Ejhieh and Kjorsandi 2010; Xu et al. 2013b).

Decomposition of Eriochrome Black T has been studied by various researchers using different nanomaterials. Kazeminezhad and Sadollahkhani (2014) found the enhanced photocatalytic degradation (88%) of dye well-crystalline anatase  $\text{TiO}_2$  under basic conditions (pH 11.0) possibly due to higher concentration of hydroxyl radicals. Using  $\text{Fe}^{3+}$ - and  $\text{Pt}^{4+}$ -impregnated  $\text{TiO}_2$  nanostructures of different shapes, Eriochrome Black T could be successfully photodegraded (82%) within 90 min under UV light irradiation (Kansal et al. 2013b). A possible degradation pathway of the dye is depicted (Bonamali et al. 2016) in Fig. 7.

### Indigo carmine

Indigo carmine is highly toxic indigoid dye and widely used as a microscopic stain in biology, an additive in

pharmaceuticals as well as redox indicator in analytical chemistry. Being the most widely used textile dyeing agent, it constitutes one of the largest groups of pollutants in water and hence responsible for damaging the aquatic life (Othman et al. 2007; Julkapli et al. 2014).

Under blue-light irradiation, nanofibers of CdS showed better photocatalytic activity (Hernández-Gordillo et al. 2015) as compared to commercial CdS (Fig. 8). Various other nanomaterials have been successfully used as photocatalysts for removing Indigo Carmine, such as palladium-coated zinc sulfide/reduced graphene oxide (Pd-ZnS/rGO) nanocomposites (Agorku et al. 2015), platinum (Pt) and palladium (Pd) nanoparticles decorated on graphene sheets (Kurt et al. 2016) and nanometric tin dioxide-based composites. Mineralization of the dye was observed using 60% ratio of Sn/Al<sub>2</sub>O<sub>3</sub> (40 min) (Coelho et al. 2010) and Pd-ZnS/rGO nanocomposites (210 min) (Agorku et al. 2015). However, approximately 75 and 70% of Indigo Carmine were degraded within 5 min using Pt- and Pd-graphene nanocomposites, respectively (Kurt et al. 2016).

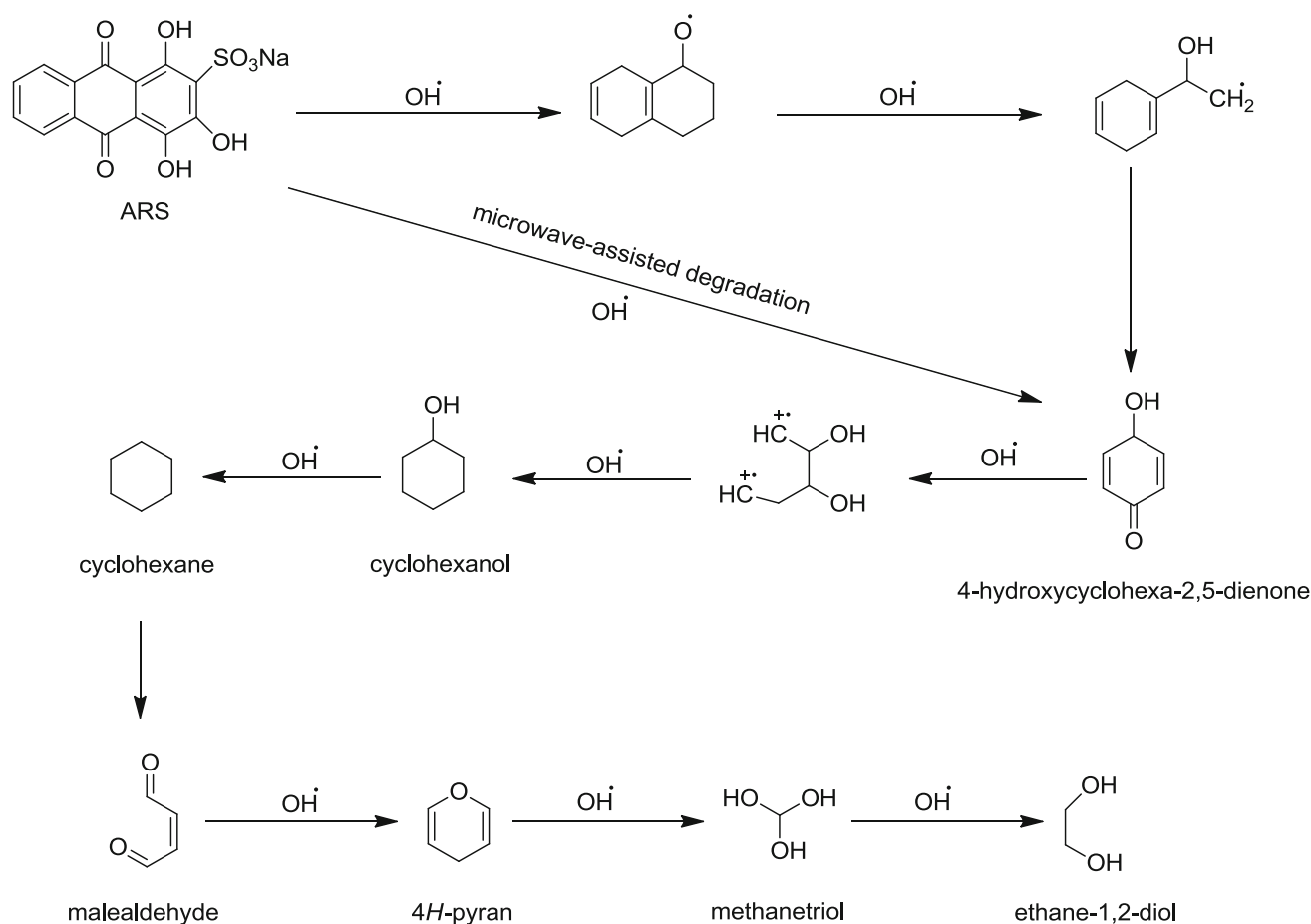
**Fig. 5** Possible degradation mechanism of eosin Y using Hes-TiO<sub>2</sub> nanoparticles (Vignesh et al. 2012)

## Cationic dyes

### Malachite green

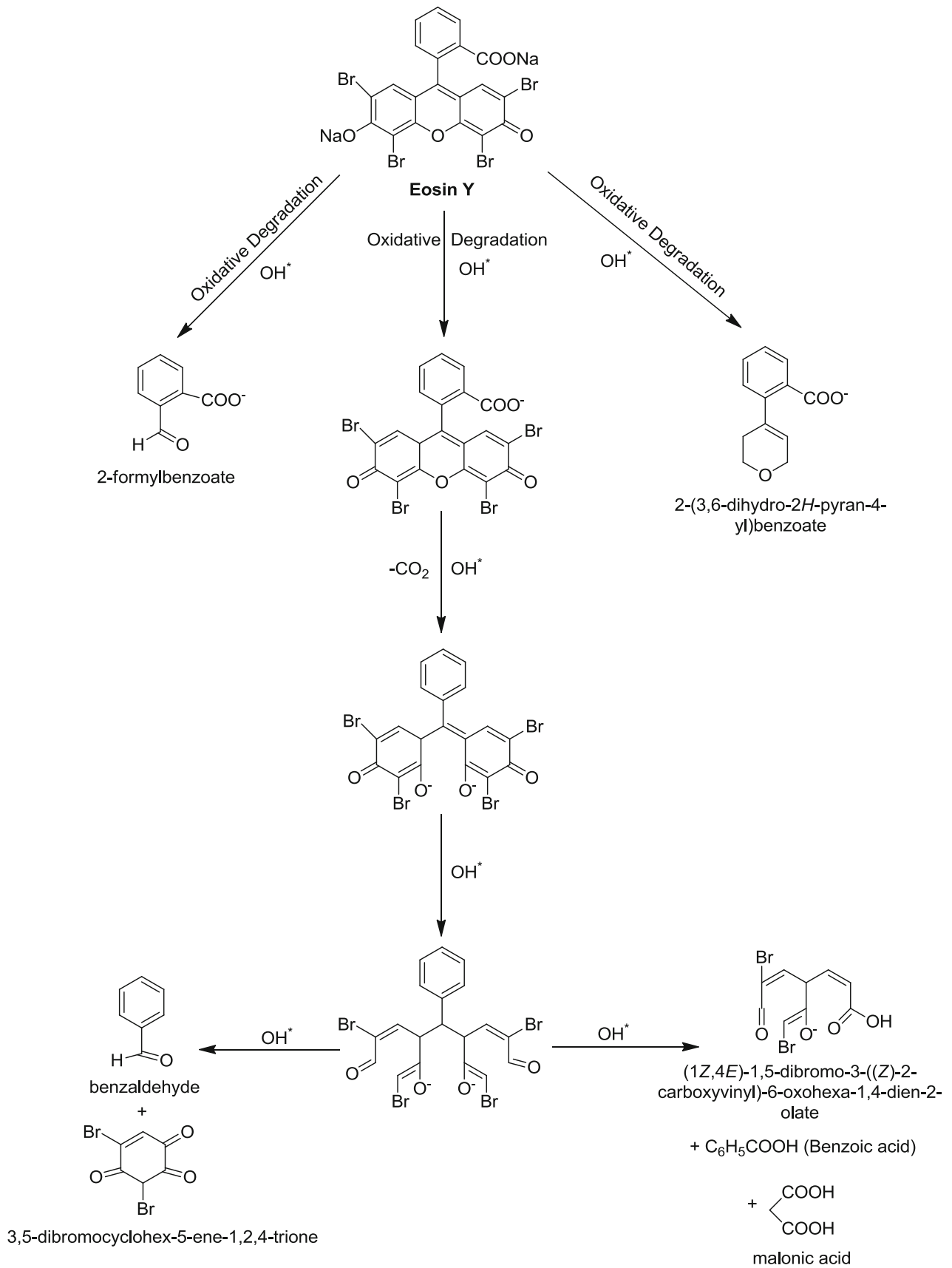
Malachite green is one of the most controversial synthetic (cationic) textile dyes (Kumar et al. 2005) because of its toxicity (Crini et al. 2007). Malachite green has widespread applications in other sectors, including food, paper and aquaculture industries. Malachite green-treated fishes show carcinogenic effects in immune and reproductive system (Srivastava et al. 2004).

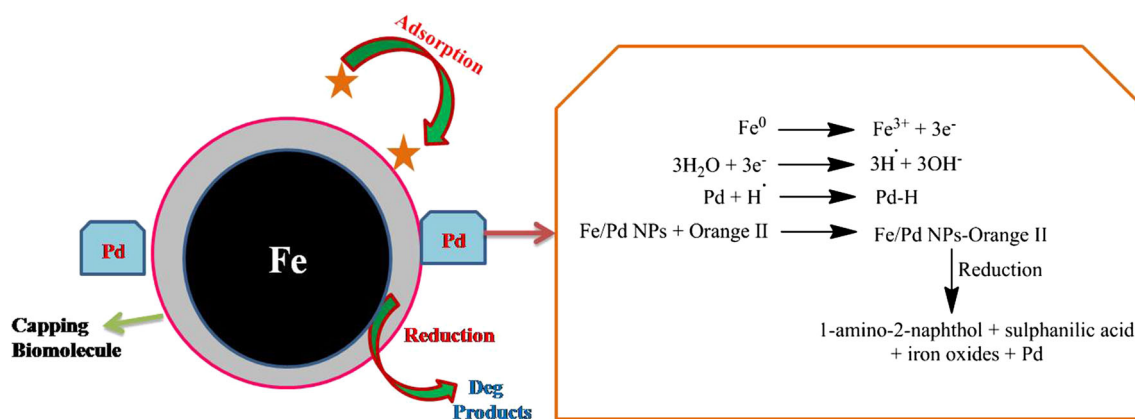
Nanosheets of MnO<sub>2</sub> were used under aerobic conditions for the maximum oxidative degradation (99%) was achieved under optimized conditions (Saha and Pal 2014). Several other nanomaterials such as iron-based nanoparticles (Huang et al. 2014) (75.5% degradation of dye), potassium zinc hexacyanoferrate nanocubes (Jassal et al. 2015b) (94.15%) and CuI-CuO nano composites (Nekouei



**Fig. 4** Degradation pathway of Alizarin red S using nanohybrid of ZnO (Riaz et al. 2016)







**Fig. 6** Conceptual model depicting the removal mechanism of *Orange II* dye using Fe/Pd nanoparticles (Luo et al. 2016)

et al. 2016) also exhibited high catalytic efficiency at neutral pH due to ion screening effects of  $\text{H}^+$  and  $\text{OH}^-$  ions in acidic and basic conditions, respectively.

### Methylene blue

Methylene blue is a thiazine dye used as an anti-malarial and chemotherapeutic agent in the aquaculture industry (Small and Hintelmann; Burhenne et al. 2008).

The dye has been degraded successfully using various nanomaterials including ZnSe/graphene nanocomposites (Hsieh et al. 2015), copper-supported clay nanocomposite (Mekewi et al. 2016), titanium dioxide (Pandey et al. 2015), thorium (IV) tungstomolybdate nanocomposite (Gupta et al. 2013b) and Ta-doped ZnO nanoparticles (Kong et al. 2010). Complete removal of the dye was obtained using Cu supported organo-treated clay (Mekewi et al. 2016), whereas the degradation efficiency of 99.6% was obtained using ZnSe/graphene nanocomposites (Hsieh et al. 2015). Kong et al. (2010) concluded that pH plays an important role in the photocatalytic degradation of the dye. Employing a green route, Jassal et al. (2016a) synthesized different potassium metal hexacyanoferrate (KMHCF) nanoparticles using *Aegle marmelos* as a natural surfactant and utilized them for the degradation of methylene blue. Highest degradation (95%) was obtained with KCuHCF followed by KNiHCF (91.4%) and KCoHCF (89.3%) nanoparticles. Nanoparticles obtained via different route or biogenic sources may have different catalytic efficiencies on the same dye. For example, silver nanoparticles (Ag) could be synthesized using individually *Moringa tinctoria* leaf extract, *Polygonum Hydropiper* and Yeast (*Saccharomyces cerevisiae*) extract. It has been observed that the time required by Ag nanoparticles for removal of methylene blue is 72 h (95% degradation under sunlight irradiation) (Vanaja et al. 2014), 13 min (mineralization) (Bonnia et al. 2016) and 6 h (90%) (Roy et al. 2015), respectively.

### Methyl violet

Methyl violet is one of the cationic dyes with high brilliance and color intensity. Methyl violet interferes in the photosynthesis of aquatic plants (Hameed 2008). Inhalation of methyl violet or absorbance through the skin causes various problems such as, respiratory tracks injury, diarrhea, pain, vomiting, headache and dizziness (Ofomaja 2008). It is mutagenic and carcinogenic in nature (Crini 2006). Methyl violet is widely used in bacteriological and histopathological works for staining purposes (Sarnaik and Kanekar 1999).

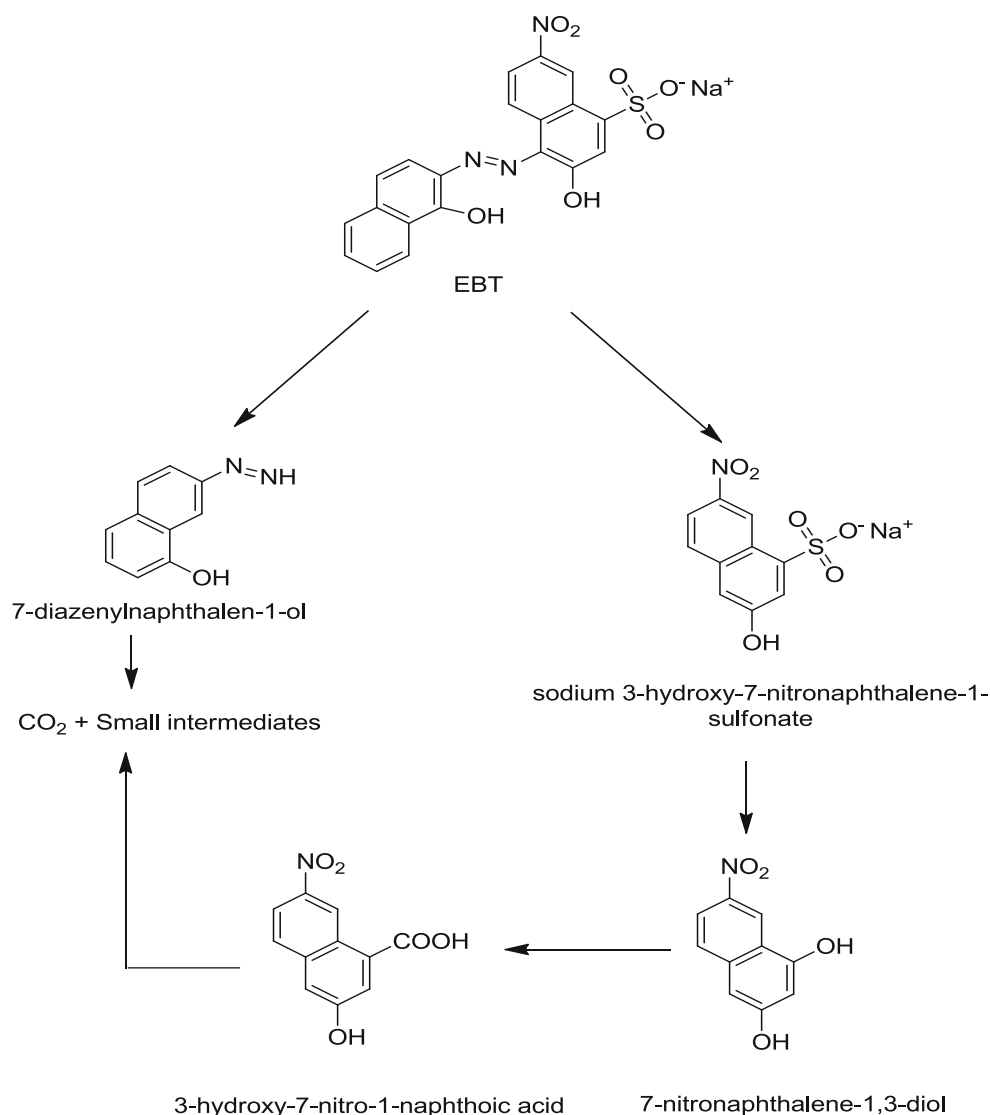
Removal of methyl violet from wastewater is an essential task, and therefore, several nanoadsorbents have been employed, for example, nanographite/ $\text{Fe}_3\text{O}_4$  composite which effectively worked under basic conditions (pH more than 10.0) because of increased negative charges which favor the interaction between cationic dye and negatively charged adsorbent (Li et al. 2014). It was observed that doping of ZnS quantum dots with  $\text{Fe}^{3+}$  ions enhanced the degradation process (more than 95% at pH 11.0) under UV radiation (Shamsipur and Rajabi 2014). The best results were obtained using ZnO nanoparticles, i.e., 100% degradation in 60 to 80 min (Jeyasubramanian et al. 2015).

### Rhodamine B

Rhodamine B is known as water tracer fluorescent and widely used colorant in textiles and foodstuff industries (Richardson et al. 2004). The adverse effects such as carcinogenic, neurotoxicity and chronic toxicity have been proven experimentally harmful toward humans and animals (Khan et al. 2011).

Removal of rhodamine B was carried out under UV as well as solar conditions using ZnO nanopowders and Ag/ZnO/graphene oxide (Ag/ZnO/GO). Solar light irradiation

**Fig. 7** Possible pathway for the photodegradation of Eriochrome Black T using Fe<sup>3+</sup>- and Pt<sup>4+</sup>-impregnated TiO<sub>2</sub> nanostructures (Bonamali et al. 2016)



gave better results (more than 95% degradation in 8 min) (Nagaraja et al. 2012), while with (Ag/ZnO/GO) almost 100% degradation was achieved under UV irradiation in 60 min (Qin et al. 2015). In addition to this, several other adsorbents were also employed for the effective removal of dye (Xu et al. 2014; Motahari et al. 2015; Qin et al. 2015). Using NiO nanomaterials, nearly 76% of the dye was removed within 30 min, which gradually increased with time (Motahari et al. 2015). BiOBr/montmorillonite composite effectively removed 98.96% of the dye within 120 min under acidic conditions (Fig. 9) (Xu et al. 2014).

### Brilliant blue-R

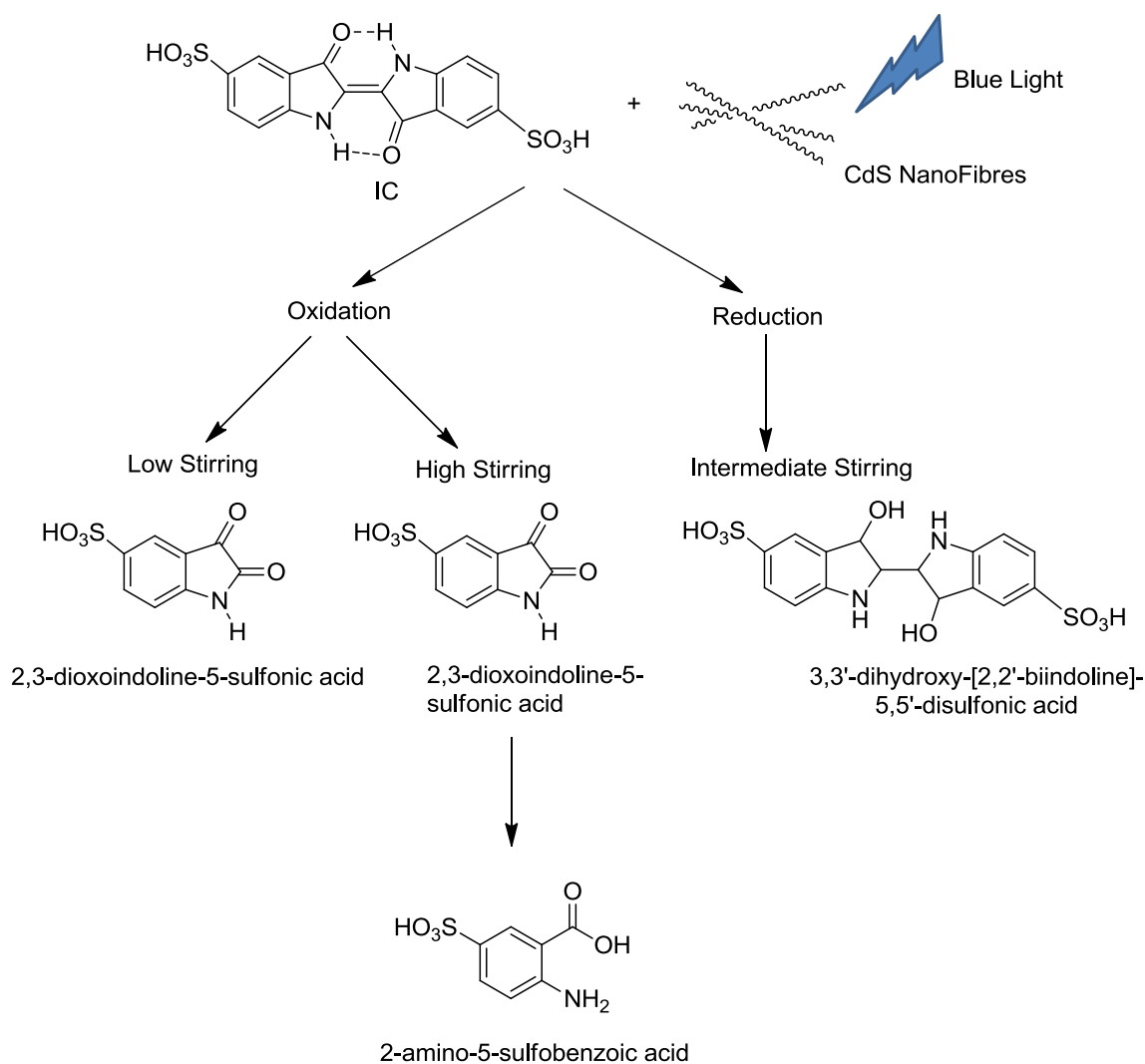
Brilliant blue-R is a triphenyl methane dye used in biological activity of proteins in analytical biochemistry. Hazardous effects of Brilliant blue-R are still not known clearly. However, exposure to Brilliant blue-R may cause

irritation to the skin, eyes, respiratory system and adverse effects to aquatic environment (Pearce et al. 2003).

Cobalt ferrite nanoparticles showed extremely fast adsorption kinetics for Brilliant blue-R. The dye was adsorbed in the range of 65–93% within one minute, and equilibrium was achieved in 60–120 min (Khan et al. 2015). Green synthesized copper oxide nanoparticles and ZnO/GO nanocomposite were also used for decolorization of the dye (Sankar et al. 2014; Kashinath et al. 2016). Degradation of Brilliant blue-R was affected by the temperature used in process. ZnO/GO nanocomposites showed better results (95.4%) as compared to non-annealed one (90.64% degradation) (Kashinath et al. 2016).

### Crystal violet

Crystal violet is one of the triphenylmethane dyes used in controlling fungal growth (Singh et al. 2011), as a



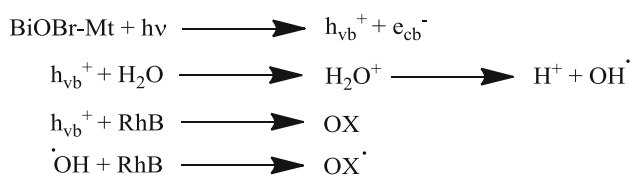
**Fig. 8** Photodegradation of indigo carmine using CdS nanofibers under blue-light irradiation (Hernández-Gordillo et al. 2015)

biological stain, dermatological agent (Ju et al. 2011) and a colored ligand in determination of dextran sulfate sodium (Hao et al. 2009). In addition, this dye is a mitotic poisoning agent in nature (Kumar and Ahmad 2011).

Various nanomaterials have used as adsorbents for removing Crystal violet dye successfully, such as CdS, cobalt-doped titania, nickel dioxide and zinc oxide nanorods (Nezamzadeh-Ejehie and Banan 2012; Preethi et al. 2014; He et al. 2010; Dil et al. 2016). Interestingly, within five minutes 97% of dye was degraded to various small products using nickel dioxide nanoparticles (He et al. 2010) (Fig. 10). Zinc oxide nanorods proved to be an effective catalyst since 99.8% of the dye was removed under optimized conditions (Dil et al. 2016). Using *Moringa oleifera* peel as a stabilizing and reducing agent, CeO<sub>2</sub> nanoparticles were synthesized and applied for the photocatalytic degradation of Crystal violet (97.5%; 1 h) (Surendra and Roopan 2016).

### Brilliant green

Brilliant green is one of the triphenylmethane cationic dyes used as an antiseptic, biological stain and shows its effectiveness toward gram-positive bacteria (Mai et al. 2008; Garg et al. 2011). The inhalation and digestion of Brilliant green is highly toxic or even carcinogenic to lungs and target organs (Kismir and Aroguz 2011; Munusamy et al. 2013). Under optimized conditions, nanoferrites of Mn<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> adsorbed 92% of the dye effectively (Hashemian et al. 2015). Graphene oxide and TiO<sub>2</sub> nanoparticles doped with alkaline earth metal ions (Sr<sup>2+</sup>) were also used as adsorbing agents (Ghaedi et al. 2014; Sood et al. 2015). Graphene oxide nanoparticles degraded 93% of the dye within 10 min (Ghaedi et al. 2014), whereas 96% of degradation efficiency was obtained using doped TiO<sub>2</sub> nanoparticles within 1 h (Sood et al. 2015).



**Fig. 9** Photodegradation pathway of Rhodamine B over BiOBr-Mt (Xu et al. 2014)

### Basic Fuchsin

Basic Fuchsin is an inflammable triphenylmethane dye and widely used in leather and textile industries as coloring agent and also possesses biological use such as staining of collagen, muscle, mitochondria and tubercle bacillus (Grimley 1964). The dye causes severe eye, skin, gastrointestinal and respiratory tract irritation (Gupta et al. 2008). Catalytic activities of Pt-graphene and Pd-graphene nanocomposites revealed that nearly 55% and 58% of the dye were degraded, respectively (Kurt et al. 2016).

### Environmental concern of hazardous dyes

After the dyeing process, the effluent (millions of tonnes) from industries such as textiles, cosmetics, paper and printing is generally dumped. Annually, the amount of discharged dyes is constantly increasing which is probably the major reason for environmental pollution. In present scenario, most of the countries are separating the dye chemicals from the wastewater. This leaves behind the problem of dye sludge and clean water that still contain traces of dyes. Moreover, the use of reactive dyes worldwide has approached to 178,000 tonnes (Phillips 1996). Currently, high production of dyes is observed, especially in the developing countries like China, which now accounts for 40–45% of the world’s total dye consumption (Franssen et al. 2010).

In Mexico and China, factories discharged the wastewater contaminated with synthetic dyes (e.g., indigo and other). This resulted in coloration of the river water (Brit 2008) and affected the health of the local residents and farmers residing nearby. In addition to this, labors exposed to dye are detected with tumors, lung and cerebrovascular disease in Japan and USA at the rate of 40 times higher than general population (Brit 2008).

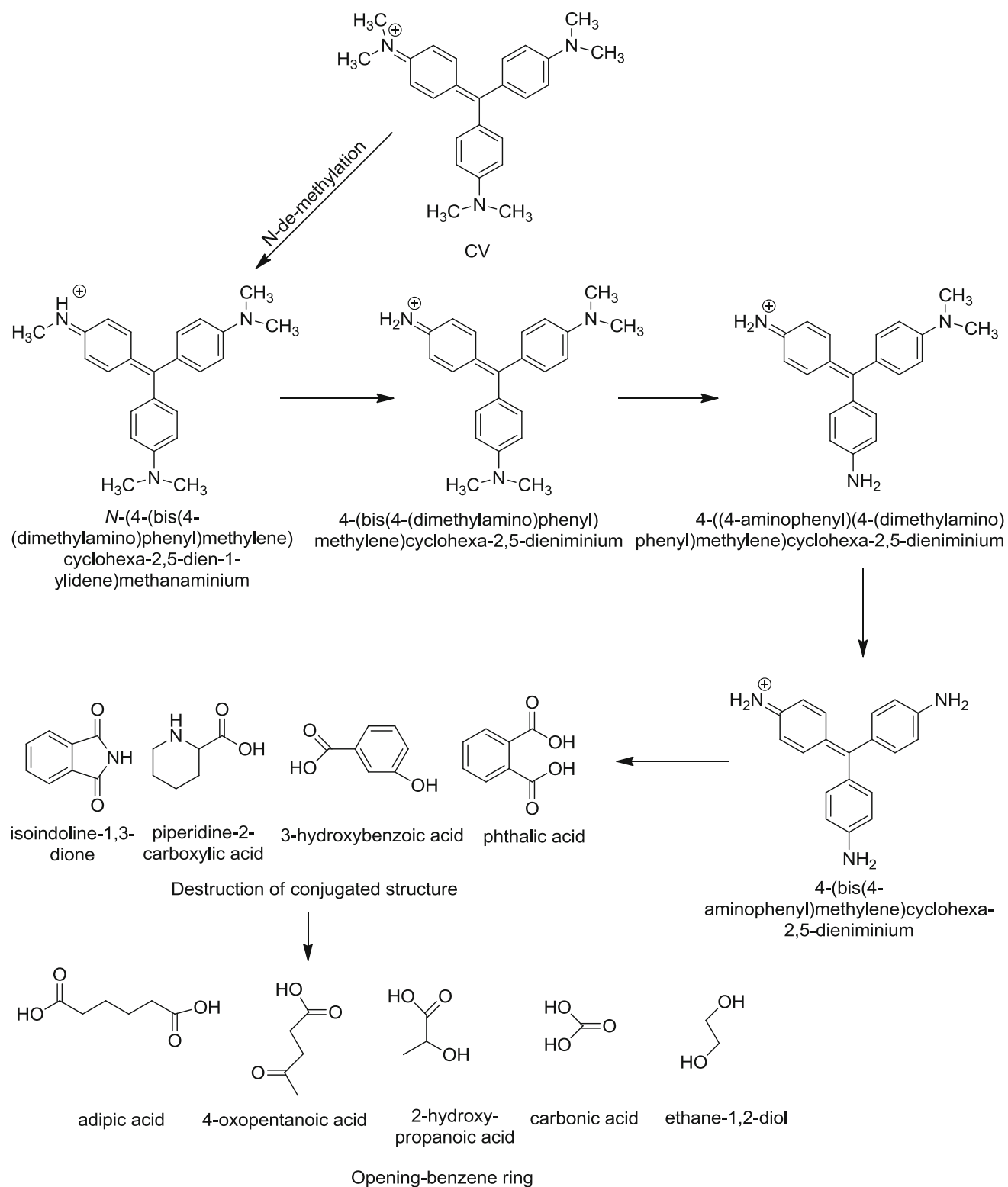
European Commission has banned many toxic azo dyes like navy blue, particularly used in leather industry (Chemical Industries Newsletter et al. 2008). In the last decade, per capita consumption or production of dyes is growing at a rapid pace in developing countries (especially China and India) than in the developed ones (Western Europe and Japan) (Chemical Economics Handbook 2015).

It has been reported that after processing around 12–20 tonnes of textiles, 3000 m<sup>3</sup> of water is let out per day (Pagga and Brown 1986; Kdasi et al. 2004). This wastewater contains large amount of dyes and other chemicals containing trace amount of harmful metals such as As, Cr, Zn and Cu. Chemicals present in water are persistent toward sunlight and do not allow the light to reach the aquatic biota, thus increasing the biological oxygen demand (BOD) and inhibiting the photosynthesis process.

### Conclusion

A number of hazardous synthetic dyes (cationic as well as anionic) have been manufactured with high production rate. Their wide use and untreated discharge from the industries are found to be the prominent sources of water pollution. The relatively high use of dyes is observed in Asian countries. To eliminate their negative impacts, the extensive use of nanomaterials was observed for oxidative degradation/removal of dyes from wastewater. In cationic dye, methylene blue, crystal violet, Brilliant blue-R and rhodamine B, while in anionic dye, methyl orange, Congo red, Alizarin red S and eosin Y, are extensively treated with nanoparticles. The use of various nanoparticles (as such or doped) like ZnO, TiO<sub>2</sub>, metallic nanoparticles (Fe, Pt and Pd) and NiO<sub>2</sub> has resulted in more or less complete degradation into non-toxic unstable by-products which ultimately undergo mineralization in a very short time. Doping could increase the catalytic potential by manifolds of the nanoparticles. Mostly, the catalytic activity of nanomaterials gets enhanced at neutral pH (due to ion screening effect) and under UV irradiation (generation of electron–hole pairs). Different catalytic efficiencies were seen for nanoparticles obtained via different biogenic surfactants. This might be due to the variable size and morphology of the nanoparticles obtained. In general, it can be concluded that owing to the high catalytic potential of these nanomaterials, these can be used as commercialized adsorbents on industrial scale.

Activated carbon and chitosan were widely used as commercial adsorbents in dye industries, but due to their high production cost there is immediate need for the commercialization alternative adsorbents with high removal efficiency. Low-cost and most efficient adsorbents in this respect are the “nanomaterials” such as ZnO, TiO<sub>2</sub>, metal oxides, and organic molecules which are capable of degrading dye completely in a very short time (few minutes to hours). New nanoadsorbents based on composites like inorganic–inorganic materials (metal oxide–metal oxide), inorganic–organic materials (metal oxides–carbon nanotube/graphene), metal oxides and their composite with



**Fig. 10** Degradation pathway of crystal violet using NiO<sub>2</sub> nanoparticles under microwave irradiations (He et al. 2010)

natural materials (metal oxide–natural polymer) may be developed to rectify the problem of dye and other organic pollutants. Keeping these points into consideration, these

nanomaterials can be used on a commercial scale, though this needs further exploration. Commercialization of nanomaterials can greatly help in solving the real-world

wastewater problem caused due to hazardous dyes. Moreover, nanomaterials used in the above studies can also be generated via green route either by employing plant-based surfactants or by using microorganisms in place of the synthetic surfactants. This will make the whole process green and will, thereby, help in the remediation of environment. Currently, a lot of researchers worldwide are working on the green synthesis of nanoparticles using plant extracts or microorganisms. Application of these nanoparticles in the degradation of harmful dyes will help in reconstructing the polluted environment.

**Acknowledgements** One of the authors Ms. Vidhisha Jassal is thankful to Ministry of Human Resource Development (MHRD), New Delhi, for providing financial assistance.

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