

Removal of dyes from wastewater by nanomaterials: A review

Wenqian Ruan¹, Jiwei Hu^{1,2*}, Jimei Qi¹, Yu Hou¹, Chao Zhou¹, Xionghui Wei³

¹Guizhou Provincial Key Laboratory for Information Systems of Mountainous Areas and Protection of Ecological Environment, Guizhou Normal University, Guiyang 550001, PR China

²Cultivation Base of Guizhou National Key Laboratory of Mountainous Karst Eco-Environment, Guizhou Normal University, Guiyang 550001, Guizhou, China

³Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

*Corresponding author: Tel: (+86) 851-8670-2710; E-mail: jiwei.hu@yahoo.com, jwhu@gznu.edu.cn

DOI: 10.5185/amlett.2019.2148

www.vbripress.com/aml

Abstract

Dyes are widely used to colour products in textile, leather tanning, cosmetics, pigment and many other industries. Effluents discharged from these industries cause potential hazards to environment and human health. Hence, the removal of dyes from water/wastewater has gained a huge attention in recent years. So far, biological, chemical and physical methods are the traditional techniques, of which adsorption is found to be a more effective and cheap method for removing dyes. Nanotechnology has applied successfully to the water/wastewater treatment and emerged as a fast-developing promising field. Application of nanomaterials (NMs) in dyes removal seems to be an efficient way. In this review, extensive literature information was presented with regard to dyes, its classification and toxicity, different methods for dyes removal including the removal of dyes by NMs. It is evident from the literature survey that NMs have shown good capability for the removal of dyes. Copyright © 2019 VBRI Press.

Keywords: Wastewater treatment, nanomaterials, graphene, dyes removal, adsorption capacity.

Introduction

Water is a precious commodity, which is an indispensable and absolutely necessary sustenance for life. Although 71 % of the earth surface is covered with water that consists of nearly 97.5 % salty water and only 2.5 % freshwater, merely 0.007 % of all water is available for drinking [1]. Industrial wastes are the major source of water pollution, which contain various kinds of dyes and other pollutants [2, 3]. Dyes have been extensively used in textile, leather tanning, cosmetics, pigment and many other industries [4-8]. The presence of these dyes in the hydrosphere possesses a significant source of pollution because of their visibility at very low concentrations and their nature of recalcitrance, which can lead to undesirable danger to the aquatic life such as reducing sunlight penetration and resisting photochemical reactions. Their waste products generated during the dyeing processes are toxic, mutagenic, carcinogenic, even increase chemical oxygen demand (COD) and biochemical oxygen demand (BOD) levels of aquatic sources, and pose a threat to the human health. [9-11]. Therefore, it is necessary to eliminate dyes from wastewater effectively prior to their final discharge to the environment.

Basically, large quantities of dyes are discharged into the environment from various industrial processes,

which have posed challenges to environmental scientists. Numerous technologies such as membrane separation, advanced oxidation, flocculation-coagulation, electrochemical techniques and aerobic or anaerobic treatment have been used in the removal of dyes from wastewater [12-16]. Therefore, there is an urgent requirement to develop an innovative and low-cost processes for the removal of dyes. Adsorption as one of the most effective methods for wastewater treatment has been successfully applied to reduce hazardous inorganic/organic pollutants present in the effluents [17]. The superiority of adsorption in comparison with the other methods are its sludge free operation and completed removal of dyes even from dilute solutions [18]. A number of adsorbents have been reported for the feasibility as low cost adsorbents to remove dyes from wastewater. Some of them are chitosan [19], wheat straw [20], wood hull [21], banana and orange peels [22], oil palm ash [23], spent tea leaves [24], degreased coffee bean [25], mango peels [26], rice husk [27], palm kernel shell [28], coconut shell [29] and fly ash [30]. However, the application of these adsorbents has been restricted because of their separation inconvenience. Thus, great efforts are needed to exploit new promising adsorbents.

The advancement of nanotechnology has attracted tremendous interest from many researchers in the scientific fields. The growing interest in nanoscience

indicates that the potential of nanomaterials (NMs) is still unexplored and yet to be addressed. Nanomaterials are of high importance that include structures and devices with the size varying from 1 to 100 nm. Because of its distinct properties, large surface area and quantum size effects, these materials can provide unprecedented opportunities (such as strong adsorption, enhanced redox, and photocatalytic properties) to treat contaminants in wastewater [31-33]. A variety of nanomaterials i.e. nano metals, nano metal oxides, graphene or graphene-based nanomaterials and polymer-based nanomaterials, have been widely applied in the removal of contaminants in wastewater [34-38]. The results demonstrated that these nanomaterials showed a high adsorption capacity.

This review has three main sections. Firstly, the types and toxicity of dyes are described. Then, the different types of methods applied in wastewater treatment are discussed. Thirdly, the adsorption of various dyes from aqueous solutions by a wide range of nanomaterials is elaborated and their maximum adsorption capacity on various dye adsorption are compared. Finally, a summary and outlook in the form of conclusions and recommendations are given for their full-scale applications.

Dyes

Dyes are basically organic compounds that can connect themselves to surfaces of fabrics to impart a colour [10]. Dyes can be classified according to their constituents, colours and applications, of which application is the most commonly used method for dyes classification [39, 40]. Azo dyes, anthraquinone dyes, phthalocyanine, indigoid dyes, nitroso dyes, nitro dyes and triarylmethane dyes based on the classification of chemical structure are presented in Table 1. Azo, anthraquinone and triarylmethane dyes are the most important groups among these dyes.

Table 1. The class of dyes based on the chemical structure [10].

Class	Chromospheres	Examples
Azo dye		Reactive black 5
Anthraquinone dyes		Reactive blue 4
Indigoid dyes		Acid blue 71
Nitroso dyes		Acid green 1
Nitro dyes		Acid yellow 24
Triarylmethane dyes		Malachite green

Table 2. Application and toxicity of different dyes [41].

Dyes	Example	Application	Toxicity
Acid	Sunset yellow, Methyl orange	wool, silk, paper, leather,	carcinogenic (benign and malignant tumors)
Cationic	Methylene blue, Rhodamine 6G	paper, modified polyesters	carcinogenic (benign and malignant tumors)
Disperse	Disperse orange 3, Disperse red	nylon, acrylic fibers	allergenic (skin), carcinogenic
Direct	Congo red, Direct red 23	cotton, paper, leather	Bladder cancer
Reactive	Reactive red 120, Reactive red 198,	cotton, wool, nylon	dermatitis, allergic conjunctivitis,
Vat	Vat orange 15, Vat orange 28,	cellulosic fibers	-

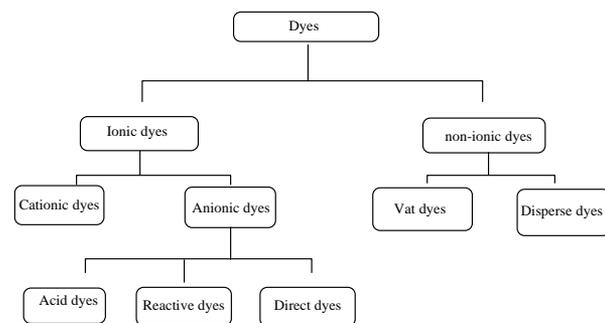


Fig. 1. Classification of dye according to the ionic charge.

The classification based on the different applications for the dyes are vat, mordant and disperse dyes shown in Table 2 [41]. In addition, dyes usually used in textile industry are cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (disperse dyes) depending on their particle charge dissolution in aqueous solutions (Fig. 1) [42, 43]. The complex structure of dyes render them ineffective in the presence of heat, light, microbes, and even oxidizing agents, which also lead to the difficulty in the degradation of the dyes. The presence of dyes in water affects sunlight penetration and oxygen solubility, which decreases the water quality and hinder photosynthesis on aquatic flora and fauna [39, 44]. Additionally, it also can cause severe damage to human health such as the increase of heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis [45].

Azo dyes

Azo dyes (monoazo, diazo, triazo, polyazo) account for the majority of synthetic aromatic dye, which are composed of one, two, three or more (N=N) groups and connected to benzene and naphthalene rings that are substituted frequently with some functional groups, e.g. triazine amine, chloro, hydroxyl, methyl, nitro, and sulphonate [46]. Azo dyes are extensively used in pharmaceutical, textile dyeing, food, cosmetics and paper printing. Approximately 80% of azo dyes are used in textile industries due to its high stability, low cost and variety in colors [47]. It was estimated that approximately 10-15% of dyes in effluents goes

unbound with the textile fibers and are released into receiving water bodies [48]. For example, the dyestuff of 30-60 g and water of 70-150 L were needed for dyeing 1 kg of cotton, and it is reported that up to 50% of used dyes were discharged into water sources by direct or indirect ways [49, 50].

Reactive dyes are azo dyes that form covalent bonds between the reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine [51]. In contrast to other classes of dyes, reactive dyes have many advantages in the textile industries because of their bright color, water-fast, simple application techniques with low energy consumption. Thus reactive dyes are the most commonly used at present. However, reactive dyes were found to be mutagenic and carcinogenic and even the intermediate products, i.e. mineralization, aromatic amine and an arylamine, also have severe adverse effects on human beings, including damages in the brain, liver, kidney, central nervous and reproductive systems [52].

Anthraquinone dyes

Anthraquinone dyes are one of common groups for dyes, which represent the second largest class of textile dyes after azo dyes and have been widely used in the textile industry owing to their wide array of color shades, fastness properties and ease of application and minimal energy consumption [53]. Another major advantage of anthraquinone dyes applied in dyeing processes is their high affinity to silk and wool. However, due to their fused aromatic structure, anthraquinone dyes exhibit a lower rate of decolorization. Most of these dyes are toxic, carcinogenic and mutagenic, therefore the removal of anthraquinone dyes has attracted an enormous attention.

Triarylmethane dyes

Triphenylmethane dyes are aromatic xenobiotic compounds that were formed by a central carbon atom connected to two benzene rings and one p-quinoid group (chromophore). The common auxochromes are -NH₂, NR₂ and -OH. These dyes have brilliant colors with typical shades of red, violet, blue and green, such as Malachite green (MG), Crystal violet (CV), Bromophenol blue (BB), etc. [54]. These dyes are widely applied in the textile industry for coloring the substrates like modified nylon, polyacrylon nitrile, wool, silk and cotton. Another important application of triphenylmethane dyes are used in paper and leather industry and gasoline [53]. Their relatively inexpensive dyeing, high tinctorial strength and the low light fastness especially in the slow washing and light are considered suitable for dyeing a wide range of textile substrates. In addition, triphenylmethane dyes have been extensively employed in medicine as medical disinfectants, because these dyes exhibit antibacterial, antifungal and antiprotozoal properties, they can be used for the disinfection of post-operative wounds and also employed in the controlling diabetes [55]. Some of these dyes (phenolphthalein, fuchsin, and fluorescein) are used as indicator dyes due to their pH sensitivity.

Dye removal techniques

A wide range of technologies have been developed and applied for the scavenging of dyes, which can be divided into three main categories: biological methods, chemical methods and physical methods [56]. High capital costs, low efficiency and generation of excess sludge limit their practical applications. Some of these methods have been found to be more versatile and superior to other techniques and are appropriate for removing a wide range of dyes in wastewater [57]. As a better alternative, adsorption offers the low initial cost, produces nontoxic by-products and completely remove dyes even from dilute solutions [58].

Biological methods

Implementation of microbial techniques is proven to be less energy intensive and most economical to treatment the industrial effluents. Microbial biosorption and biodegradation have been explored to treat the industrial effluents. Microorganisms like algae, yeast, filamentous fungi and bacteria have the potential of transforming dyes molecule into less harmful forms [59]. This property of microorganism is attributed to the cell wall components (heteropolysaccharides and lipids), which are composed of different functional groups including amino, hydroxyl, carboxyl, phosphate and other charged groups. They can cause strong attractive forces between the azo dye and cell wall [60].

Degradation of dyes by fungi

The feasibility of fungi for the degradation of various pollutants such as polyaromatic hydrocarbons, organic waste, dyes and steroid compounds have been reported [61]. This property is derived from a metabolic product by a large set of intracellular and extracellular enzymes [62]. White-rot fungi as the most widely used fungi have four main genera such as *Phanerochaete*, *Trametes*, *Bjerkandera* and *Pleurotus*. The ligninolytic enzymes produced by white rot fungi play vital roles in dye removal due to their nonspecific enzyme systems [63]. *Phanerochaete chrysosporium* used for dye decolorization was first introduced by Tien and Kirk [62]. Wu *et al.* reported that *Phanerochaete chrysosporium* decolorize Reactive red 22 (RR 22) dye up to 100% after 30 hours of treatment [64]. Several other white rot fungus (*Trametes trogii*, *Trametes versicolor* and *Pleurotus sajor-caju*) were used for the degradation of dye in effluents [50, 65, 66]. However, the limitation for the application of the fungal to decolorize dyes is the long hydraulic retention time required for complete decolorization and the preservation of fungi in bioreactors is also a matter for consideration [67, 68].

Degradation dyes by yeasts

Although only few studies have investigated the decolorization and degradation ability of yeasts, they can serve as an attractive alternative for removal of textile

dyes because of its rapid growth like bacteria and the capacity to sustain in adverse environmental conditions even at low pH. Recently, Yang *et al.* reported that *Candida tropicalis* has a role in the decolorization of Reactive black 5 (RB 5) up to 99% after 48 h [69]. In addition, *Kluyveromyces marxianus* IMB3 has also shown bioaccumulation of remazol black-B with the removal efficiency of 98% after 24 h [70]. Kwasniewska *et al.* stated that Crystal violet could be decolorized effectively by *Rhodotorula rubra* [71].

Degradation dyes by bacteria

A study focused on the isolation culture of *Bacillus subtilis* was started in the 1970s [72]. Bacteria are easy to cultivate and grow rapidly so that they are suited fine for decolorizing and mineralizing azo dyes. The process for biodegradation of azo dyes occurs under conventional anaerobic, aerobic or facultative anaerobic conditions by the diverse groups of bacteria. Generally, the mechanism of bacterial degradation of azo dyes begins with the reductive cleavage of azo bonds ($-N=N-$) with the help of azoreductase enzymes (Fig. 2). Xiao *et al.* described a high capacity (94%) for the decolorization of Naphthol green B by *Shewanella oneidensis* MR-1 under anaerobic conditions [73]. Similarly, *Pseudomonas sp.* and *Enterobacter EC3* were used for degradation of Reactive blue 13 (RB 13) and Reactive black 5 (RB 5) after 70 h and 36 h, respectively (83.2% and 93.6%) [74, 75]. Furthermore, several studies also show that bacteria species are able to uptake dyes under aerobic conditions. *Aeromonas hydrophila* can decolorize Reactive red 141 (RR 141) and the decolorization is up to 80% after 24 h (Table 3) [76].

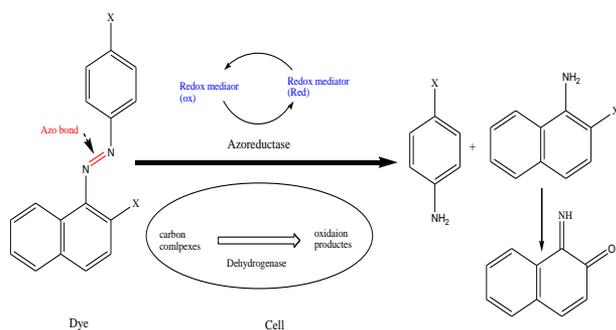


Fig. 2. The possible mechanisms of azo dyes removal by bacteria [77].

Chemical methods

Chemical methods include coagulation-flocculation, ozonation, photocatalytic degradation, electrochemical treatment, precipitation-flocculation with $Fe^{2+}/Ca(OH)_2$. These chemical techniques are efficient for the removal of dyes from wastewater, but the excessive use of chemicals cause the difficulty of sludge disposal, and the possibility of a secondary pollution problem. In addition, high electrical energy and high cost are needed for these techniques resulting in the limited use.

Table 3. Decolorization of various azo dyes by different microbial types.

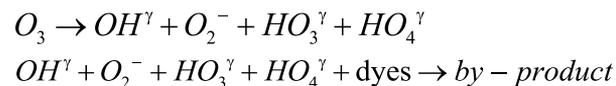
Microbial types	Dyes	Percentage removal (%)	Time	References
(4) fungi				
<i>Phanerochaete chrysosporium</i>	Reactive red 22	90-100	30 h	64
<i>Trametes trogii</i>	Anthraquinone blue	88	4 h	65
<i>Trametes versicolor</i>	Gryfalan black RL	59	400 min	50
<i>Pleurotus sajor-caju</i>	Reactive yellow 15	100	100 day	66
(5) yeasts				
<i>Candida tropicalis</i>	Reactive black 5	>99	48h	69
<i>Kluyveromyces marxianus</i> IMB3	Remazol black-B	98	24h	70
<i>Rhodotorula rubra</i>	Crystal violet	>99	4 day	71
(6) bacteria				
<i>Shewanella oneidensis</i> MR-1	Naphthol green B	94	24 h	73
<i>Pseudomonas sp.</i>	Reactive blue 13;	83	72 h	74
<i>Enterobacter EC3</i>	Reactive black 5	93.6	36	75
<i>Aeromonas hydrophila</i>	Reactive red 141	80	24	76

Coagulation-Flocculation

Coagulation and flocculation as an essential and efficient way is usually employed for drinking water treatment, textile wastewater treatment and partly reducing COD. The feasibility of this method in wastewater treatment has been tested by Sanchez-Martin *et al.* [78]. The coagulation process is the destabilization of colloids by the addition of a coagulant to neutralize the negative charges and larger particles is gathered by flocculation to form microflocs, which can be removed in subsequent sedimentation or flotation stages [79]. An agent that causes a liquid or sol to coagulate is called coagulant. Coagulants are divided into two main types coagulants and coagulant aid. Coagulants are either metallic salts, polymers or naturally occurring materials. The removal of dyes by aluminium sulphate and polyaluminium chloride have been reported [80, 81]. Khayet *et al.* stated that the effectiveness of aluminium sulphate for the removal of Acid black 210 (AB 210) is more than 90% under the condition of 40 mg/L for dosage, 4-8 range for pH and 35 mg/L for dye concentration [80]. $MgCl_2$ shows an excellent performance (98%) for the removal of MG at final pH of 10.89 and concentration of 3000 mg/L [82].

Ozonation

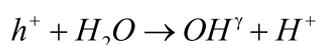
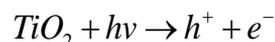
Ozone is a strong oxidative action substance, which can quickly decompose into oxygen and free radicals. The latter is combined with the dyes resulting in the destruction of color.



Ozone can attack on the pollutants via direct or indirect reactive path. The direct ozonation corresponds to the ozone molecular activity, and the indirect one is due to the highly oxidative free radicals. The decomposition rate of ozone is affected by pH and initial dye concentration. At low pH, the ozone is available as molecules to react with dye as an electrophile and at high pH, ozone can decompose automatically into hydroxyl radicals in solution, which are a powerful, effective, and nonselective oxidizing agent [83]. Shaikh *et al.* reported that the decolorization efficiencies of Reactive orange 7 (RO 7), Reactive blue 19 (RB 19), and Reactive black 5 (RB 5) were almost 100% [84]. As an example of RO 7, the percentage of colour removal was 19, 50, 60, and 75% at pH 4, 7, 9, and 11, respectively. The similar trend can be noted in the decolorization of RB 5 when the pH reached 11. The results are consistent with the finding that O^3 decomposition and OH radicals production all occurred at higher pH values, which support the performance of decolorization. The research investigated by Manali and coauthors demonstrated that the degradation of Methylene blue (MB) was up to 94.6% after 26 min [85].

Photocatalytic methods

The use of advanced oxidation processes (AOPs) for the effective oxidation of a wide variety of organics and dyes have gained special attention in recent years, due to the generation of the highly reactive hydroxyl radicals. AOPs include UV/ H_2O_2 , Fenton and photo-Fenton processes (Fe^{2+}/H_2O_2 and $Fe^{2+}/H_2O_2/UV$), the ultrasonic process, photocatalysis and electrochemical processes. Among them, priority is given to photocatalytic degradation with respect to the high efficiency and low energy consumption. Photocatalysts contain various types such as titanium dioxide, zinc oxide, perovskites and titanates. Titanium dioxide (TiO_2), used as the photocatalyst, is owing to the photogeneration of charge carriers (electrons and holes). TiO_2 is semiconductor with the band gap of 3.2 eV, which can be irradiated by ultraviolet (UV) and visible light. Upon the exposure of the photocatalyst to radiation, electrons (e^-) on the surface of TiO_2 are excited to the conduction band (CB), and positive holes (h^+) are produced in the valance band (VB) [86]. The positive hole can oxidize water to generate hydroxyl radical and the electron can reduce molecular oxygen in the solution. The photocatalytic mechanism can be described as follows:



TiO_2 as one of the most widely used photocatalysts is because of its non-toxic, inexpensive, highly stable and reactive nature. The remediation of contamination by TiO_2 can be mineralized completely to non-toxic substances such as CO and HCl. Moreover, the reaction

can take place at room temperature due to its strong oxidizing power. Seyyedi *et al.* studied UV/ TiO_2 for the removal of Direct black 38 (DB 38) [87]. The results showed that the decolorization process was sensitive to pH, so the pH of the solution is a significant factor on the removal efficiency. The percentage of degradation is more effective at acidic pH, because the isoelectric point of TiO_2 is 6.6. When the pH was lower than that of the isoelectric point, TiO_2 surface will be positively charged while the dye molecules due to having the sulfonic groups (SO_3^-) are negatively charged. With the decolorization efficiency of 90%, the optimum condition for the decolorization of DB 38 in this process was obtained at pH of 5, concentration of 0.75 g/l for TiO_2 , concentration of 26.56 mM for H_2O_2 and dye concentration of 50 ppm (Table 4).

Table 4. The removal of dyes by different chemical methods.

Chemical methods	Dyes	Removal efficiency (%)	References
(1) Coagulation-Flocculation			
Aluminium sulphate	Acid red 398	97.8	80
Polyaluminium chloride	Acid red 398	95.3	81
$MgCl_2 \cdot 6H_2O$	Malachite green	98	82
(2) Ozonation			
Ozone	Reactive orange 7	100	84
	Reactive blue 19	100	
	Reactive black 5	100	
	Methylene blue	94.6	85
(3) Photocatalytic			
UV/ TiO_2	Naphthol green B	94	87
UV/ CaO	Indigo carmine	100	87
UV/Ni-doped TiO_2 thin film	Ponceau S	73.8	88
UV/ ZnO (MCA-15 min)	Reactive black 5	96	90
(4) Electrochemical method			
Iron	Directivered	99	95
Polypyrrole	80		
Boron doped diamond			

Nano structured Ni-doped TiO_2 thin films were prepared using chemical bath deposition method by Marathe *et al.* [88]. These materials are 26.2 nm for crystal size, 92 nm nano spherical morphology of average particle size and 3.5 eV for the band gap. Nano structured Ni-doped TiO_2 thin films were prepared using chemical bath deposition method by Marathe *et al.* [88]. A series of experiments performed by Marathe *et al.* reveal that the removal efficiency of Ponceau S dye under the UV light irradiation is higher than that of Ponceau S dye under the sunlight, and the presence of a catalyst in the reaction is proven more efficient than that the absence of catalyst for both UV light and sunlight conditions [88]. Veeranna and coauthors reported the photocatalytic degradation of Indigo carmine dye using

calcium oxide (CaO) with different light source radiation [89]. Comparisons were made among visible light, long UV light and short UV light. It was found that this dye can be effectively degraded at short duration using short UV light in contrast with visible and long UV region. This finding obviously demonstrated that lower wavelength radiation presented excellent performance in photodegradation due to the benefit of higher energy.

Zinc oxide (ZnO) has attracted a significant attention because its photodegradation mechanism is similar to that of TiO₂. ZnO was applied in room-temperature UV lasers, sensors and photocatalysis owing to its unique electrical and high optical activity, high chemical stability, good photo- electric and piezoelectric behaviors [90]. Zaharieva *et al.* synthesized ZnO by classical precipitation procedure, then treated with mechanochemical method under different milling time to obtain nano-sized particles [90]. The mechanochemical treatment of ZnO materials for 0, 15, 30 and 240 min were used for degradation of Reactive black 5 (RB 5) dye under UV light. The results showed that the highest photocatalytic efficiency (96%) was achieved by the mechanochemically activated ZnO powder for 15 minutes, but the lowest degree of degradation (82%) for RB 5 dye was observed by using the mechanochemical treatment of ZnO materials for 4 hours.

Electrochemical methods

Electrochemical methods have attracted greater attention in recent years owing to its completed decolorization, operating under moderate pH range, low final temperature, reduced COD and BOD₅ as well as no sludge formation [91, 92]. Although electrochemical treatment is used for the synthesis of compounds or metals recovery, applications in the decolorization of dyes grow rapidly. In electrochemical processes, organic and toxic pollutants are destroyed by either direct or indirect oxidation process. In a direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction [93]. In an indirect oxidation process, strong oxidants (i.e. hypochlorite/chlorine, ozone, hydrogen peroxide) are generated during electrolysis, then destroying the pollutants in the solution by the oxidant generated during the oxidation reaction process [94]. Lopes *et al.* used three different anode materials (iron, polypyrrole and boron doped diamond) for the removal of Direct red 80 (DR 80) showing the removal efficiency of 99% for these materials [95].

Physical methods

Different physical methods have been developed for the removal of contaminants including membrane-filtration (reverse osmosis, electrodialysis, nano-filtration), ion exchange and adsorption. The major restrictions of the membrane filtration processes are that they need periodic replacement and have a potential problem with membrane fouling. Adsorption techniques serve as an

attractive alternative for the treatment of contaminated waters due to its cheapness, simple design and easy operation, high efficiency, no effect by toxic substances and low costs.

Membrane filtration

Membrane filtration as a means of purification or concentration like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), is an advanced treatment technology to remove color, BOD and COD. The principle of this procedure is that the pore size of the membrane is determined if the particles are passed through or retained on the side of barrier [96]. When particles are larger than the pore size of membrane, particles will be hindered to pass through.

UF can be used to separate particles, ranging from 0.05 to 0.15 μm , which are suitable for treating the inorganic particles or organic colloids due to its pore size. The experiments using UF membranes were carried out to remove Reactive black 5 by Alventosa-de Lara *et al.* [97]. The results showed that the rejection remained above 70% at dye concentration of 500 mg/L. Hence, UF membrane is not suitable for dye removal. Pore size in the range of 1 to 10 angstrom belongs to NF membrane that is enough to separate particles with nanometre in diameter. NF technology is the combination of UF and RO that presents superiority in contrast with UF and RO in terms of higher permeation of flux, higher retention of multivalent salts, relatively low investment and low operation and maintenance costs [98]. NF with cellulose nanocrystals has proven to be quite effective filtration technology for the removal of dyes such as Methylene blue (MB), Victoria blue (VB) and Methyl violet (MV) [99]. A study was carried out by Amin *et al.* to investigate the NF for treating Reactive black B (RB 5) from dye-house effluents under various operating condition of pressure, flow rate, and temperature [100]. It was found that the optimum condition was operating pressure of 15 bar, temperature of 35°C and flow rate of 480 L/h with the rejection of dye exceeding 99%. The results illustrated that nanofiltration is a highly efficient technique in the removal of reactive dyes.

Ion exchange

Ion exchange membrane has received a wide interest with high efficiency, low costs and its attractive feature for the application of water purification, heavy metals removal and textile effluents treatment. The ion exchange process can effectively remove dyes from aqueous solutions through strong interactions between charged dyes and functional groups on ion exchange resins. Classification of resins can be defined as four main categories: anion exchange membrane, cation exchange membrane, cross-linkage membrane and other ion exchange membrane. Among them, anion and cation are the most commonly used membrane for the dyes removal. Anion exchange membrane presents positively charged groups, for example, $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}^{3+}$ and $-\text{PR}^{3+}$, which are beneficial to pass anions but

prevent cations. Cation exchange membrane contains negatively charged groups, such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $-\text{PO}_3\text{H}^-$, $-\text{C}_6\text{H}_4\text{O}^-$, which allow the cations to pass but reject anions to pass [101].

The removal efficiency of anionic dye Congo red (CR) from aqueous solutions using an anion exchange membrane (EBTAC) has been investigated by Muhammad *et al.* [102]. The influence was studied for several factors including contact time, membrane dosage, ionic strength and temperature. The results indicated that contact time and membrane dosage have a significant impact on the CR removal efficiency. Nevertheless, the effect of ionic strength and temperature on the CR removal has little impact. Akazdam and Chafi extended their studies towards using the macroporous strongly basic anion exchange resin for the removal of Acid orange 7 dye (AO7) [103]. They investigated the efficiency of AO 7 by a series of experiments including various parameters, viz. contact time, pH, initial dye concentration, adsorbent dosage, agitation speed, and solution temperature. The authors noted that the solution pH has an important impact on the extent of this process. The resin could almost remove up to 75% of AO7 within 100 min. Results indicate that the experimental data was fitted well to the Langmuir isotherm model with the maximum adsorption capacity 200 mg/g. Adsorption kinetics showed that the adsorption process followed pseudo-second-order model and thermodynamic studies further confirmed that the adsorption of AO7 on the macroporous basic anion exchange resin under the investigated conditions was an spontaneous and exothermic process.

Adsorption

Adsorption is a phenomenon that the interface between gas/ liquid molecules are concentrated on the surface of porous solid. The accumulation substance at the interface is called as adsorbate, which contacts with a solid is called adsorbent [104]. The adsorption process generally can be divided into two types, physical sorption and chemical sorption with regard to how the adsorbate species is adsorbed onto the adsorbent surface. In the physical adsorption, the adsorbate sticks to the adsorbents via weak physical force controlled like Van der Waals forces, hydrophobicity, hydrogen bonding, polarity, static interactions, dipole interactions and π - π interactions [105]. In the chemical adsorption, adsorbates are chemically bound to the surface of an adsorbent by the force of the electrons exchange. Adsorption method as an attractive alternative are widely used for environmental remediation purpose, because they have been found to be superior to other methods for dyes removal from the wastewater considering flexibility and simplicity of design, cost and high efficiency. In addition, adsorption does not generate hazardous substances and avoid the secondary pollution. Adsorption by eco-friendly and cost effective adsorbent was selected for adsorption process depending on the adsorption capacity, surface area and potential for reuse cost of the materials [106].

Activated carbon (AC) is well known for their porous structure with high surface area ranging from 500 to 2000 m^2/g and its great adsorption capacities towards various kind of pollutants. These excellent properties are attributed to the source of natural materials. However, these natural material (wood and coal) are relatively expensive so that searching for renewable and cheaper precursors are indispensable. Agricultural byproducts and waste materials are the main sources for the production of AC, such as chitosan, banana and orange peel, oil palm ash, spent tea leaves, degreased coffee bean. A study by Tan *et al.* reports the removal of MB by activated carbon prepared from coconut husk [107]. The equilibrium was achieved at 30h, the adsorption capacity decreased from 434.78 to 384.62 mg/g with increase in temperature from 30 to 50°C demonstrating the exothermic nature of the adsorption reaction. From the Langmuir isotherm results, the maximum adsorption capacity of MB removal onto adsorbent (with relatively high surface area of 1940 m^2/g and total pore volume of 1.143 cm^3/g) is 434.78 mg/g . The ability of activated carbon prepared from rattan sawdust for the adsorption of MB was investigated by Hameed *et al.* [108]. The kinetic data were found to be in agreement with the pseudo second - order kinetics and equilibrium was achieved in less than 24 h. The equilibrium data followed the Langmuir model, showing the monolayer coverage of dye molecules at the outer surface of sawdust carbon.

Table 5. The removal of dyes by different physical methods.

Physical methods	Dyes	Removal efficiency (%)	References
(1) Membrane filtration			
ultrafiltration	Reactive black 5	70	97
nanofiltration	Reactive black 5	99	100
(2) Ion exchange			
anion exchange membrane (EBTAC)	Conger red	98	102
basic anion exchange resin	Acid orange 7	75	103
(3) Adsorption			
activated carbon prepared from coconut husk	Methylene blue	434.78	107
activated carbon prepared from rattan sawdust		294.12 mg/g	108

Adsorption of dyes by different nanomaterials

The growing interest in nanoscience indicates that the potential of nanomaterials (NMs) is still unexplored and yet to be addressed. Nanosized metal or metal oxide-based materials as another inorganic nanomaterials are used broadly for the removal of dyes. Nanosized metals or metal oxides, including nano zerovalent iron [109], nano zerovalent zinc [110], magnetic Fe_3O_4 [111], magnesium oxid (MgO) [112], titanium dioxide (TiO_2) [113], zinc oxide (ZnO) [114], provide high surface area and specific affinity. Especially for metal oxides, these materials have a minimal environmental impact, low solubility, and no secondary pollution. Given these superiority, they have also been selected to remove heavy metals.

Nano zerovalent iron

Nano zerovalent iron (nZVI) particles have a high efficiency in eliminating a variety of pollutants, such as nitrates, organochlorine pesticides, chlorinated compounds, heavy metals and dyes [115-118]. It is assumed that the reactivity of core-shell nanoparticles of ZVI is driven by the oxidation of the Fe^0 core in comparison with their microscale counterparts, the higher reactivity of the nanoscale particles has been attributed to the greater density and higher intrinsic reactivity of their reactive surface sites.

Rahman *et al.* reported the use of nZVI for the removal of three azo dyes, namely Sunset yellow, Acid blue A and Methyl orange [119]. The removal efficiency of these three dyes in relation to the nZVI dosage demonstrated that increasing the dosage of nZVI particles was in favor of the decolorization of the dyes. Nonetheless, the percentage of degradation decreased with increasing concentration of dyes. The influence of the change in pH on the removal efficiency of dyes illustrated that the acidic condition was favorable to the adsorption. This result may also be ascribed to the electrons of iron particles donated to H^+ ions causing the formation of atoms. These atoms induce the cleavage of the chromophore group and conjugated system in dyes with the decrease of pH [120]. The results demonstrated that the decolorization efficiency of Sunset yellow, Acid blue A, and Methyl orange by nZVI exhibits an high efficiency. Then, this material was used for the removal of Reactive black 5, Reactive red 198 and Light green, which still presents satisfactory performance of these dyes removal [109, 121]. Reactive black 5 and Reactive red 198 at initial concentration of 100 ppm were completely removed by adding 500 mg nZVI. In addition, the removal efficiency of light green dye is 97% (Table 6).

Table 6. The removal efficiency of azo dyes with nZVI.

Dyes	Example	Application	Toxicity
Acid	Sunset yellow, Methyl orange	wool, silk, paper, leather,	carcinogenic (benign and malignant tumors)
Cationic	Methylene blue, Rhodamine 6G	paper, modified polyesters	carcinogenic (benign and malignant tumors)
Disperse	Disperse orange 3, Disperse red	nylon, acrylic fibers	allergenic (skin), carcinogenic
Direct	Congo red, Direct red 23	cotton, paper, leather	Bladder cancer
Reactive	Reactive red 120, Reactive red 198,	cotton, wool, nylon	dermatitis, allergic conjunctivitis,
Vat	Vat orange 15, Vat orange 28,	cellulosic fibers	–

Nanomaterials with magnetic properties

Iron as one of highly reactive metal element can exist in variable oxidation states, which allow it to coordinate with other elements. The three commonly used oxide forms in nature are magnetite (Fe_3O_4), hematite ($\gamma-Fe_2O_3$) and maghemite ($\alpha-Fe_2O_3$) [122, 123]. Based on their

high ratio of surface area to volume, high magnetic susceptibility and excellent biocompatibility, these materials are more conducive to being re-collected and have extensive applications [124]. Bare magnetite nanoparticles have the tendency to oxidation by air and aggregation in aqueous systems [125].

Peng *et al.* used humic acid (HA) to coat on Fe_3O_4 nanoparticles to remove Rhodamine B (Rh B). HA prevented Fe_3O_4 nanoparticles from being oxidized and enhanced its stability [126]. The results for adsorption of the Rh B onto Fe_3O_4/HA illustrated that it reached equilibrium within 15 min, and the maximum adsorption capacity is 161.8 mg/g. HA coated Fe_3O_4 nanoparticles were able to remove over 98.5% of Rh B at optimized pH. Chaudhary and co-workers have fabricated Fe_3O_4 nanomaterials through chemical precipitation method using cetyltrimethylammonium bromide, as a surfactant to remove Acridine orange (AO), Coomassie brilliant blue R-250 (CBB) and Congo red (CR) [127]. A high removal efficiency was achieved at the pH of 4 for CBB, 6 for AO and CR and the amount dosage of 0.02 g. The adsorption potential of impregnated magnetic nanoparticles onto maize cobs for Methylene blue (MB) removal was studied by Tan and coauthors, which showed favorable adsorption behaviour for MB with the removal efficiency of 99.9% [128]. Surface modification of IONPs can also be achieved using other materials such as ionic liquids, polyacrylic acid and silica-based cyclodextrin (AI-CD-MNPs). Reactive red 120, Rhodamine 6G and Direct blue 15 were removed successfully by using these materials [129-131].

Nano magnesium oxide

Nanosized alkaline earth metal oxides, in particular magnesium oxide (nano-MgO), are an interesting multifunctional and exceptionally important material, which has been extensively used as a destructive adsorbent for the removal of many toxic chemicals due to their high surface reactivity and adsorption capacity [132-134]. Additionally, this material is utilized as catalyst support, toxic-waste remediation, refractory as an additive, paint and superconducting products based on the excellent optical, electrical, thermodynamic, mechanical, electronic, and special chemical properties. This material was also explored as bactericides and adsorbents [135-137]. In a study performed by Jamil *et al.*, MgO nano particles were shown to be an effective sorbent for Reactive black 5 (RB 5) and Reactive orange 122 (RO 122). It was found that the maximum adsorption capacities for RB 5 and RO 122 are 500 mg/g and 333.34 mg/g, respectively [138].

Recently, enormous efforts have been made to synthesize MgO with enhanced surface area with varying morphologies such as rods, wires, belts, tubes. Studies were performed by Dhal *et al.* on the ability of MgO nanomaterials with different morphologies (MgO nanorods, hierarchical nanostructures and nanoflakes) to act as adsorbents for the removal of toxic dyes, viz. Malachite green and Congo red [139]. A comparison of three materials (MgO nanorods, hierarchical

nanostructures and nanoflakes) for removal of these dyes illustrated that the hierarchical MgO nanostructures exhibited excellent adsorption performance for removal of both the dyes with maximum sorption capacities of 1205.23 mg/g and 1050.81 mg/g, respectively, which were considerably higher than those of other adsorbents. We can explain the higher adsorption capacity of MG and CR by the hierarchical MgO nanostructures on the basis of the probability of its high surface area and hierarchical structures.

The modification of nano MgO form an advanced composite material, which are essential to enhance dyes removal capacity. One example is the synthesis of MgO encapsulated activated carbon nanoparticles by Daniel and coauthors. This material was used as the adsorbent for the removal of Rhodamine B (Rh B) [140]. It was found that Langmuir isotherm gives a better explanation of the adsorption process with the maximum adsorption capacity of 16.2 mg/g at pH of 6.75, dosage of 100 mg and contact time of 2 h. Rice straw charcoal/MgO nanocomposites were prepared using modified coprecipitation method by Moazzam *et al.* [141]. A series of adsorption experiments were carried out to investigate the ability of rice straw charcoal/MgO nanocomposite to remove Reactive blue 221 (RB 221) from aqueous solutions by varying the amount of shaking time, adsorbent dose, shaking speed, pH, temperature and initial adsorbate concentration [141]. The optimum adsorption was found to be at adsorbent dose of 250 mg, shaking speed of 200 rpm, pH of 7.0, shaking time of 90 min, temperature of 26°C and initial adsorbate concentration of 30 mg/L. The adsorption of this dye followed the pseudo first-order kinetics and the Freundlich isotherm. The maximum adsorption capacity from the Langmuir isotherm was calculated to be 27.78 mg/g. The results indicate feasible adsorption of RB-221 on nanocomposite of rice straw charcoal/MgO nanocomposite from aqueous solutions.

Graphene oxide and graphene oxide based nanomaterials

Graphene is the two-dimensional nanomaterial with a few layer densely packed in six-membered rings of sp^2 carbon atoms, which presents remarkable properties, such as high surface area (with a theoretical value of specific surface area at 2630 m^2/g), strongly mechanical properties, electrical properties and chemical stability [142-145]. Accordingly, it has the potential of applications in nano-electronic devices, sensors, and nanocomposite materials [141]. Additionally, the graphitized basal plane structure render it to have strong π - π stacking interaction with the aromatic moieties present in various dyes [141]. Graphene oxide (GO), the functionalized graphene, contains oxygen-rich functional groups on its surface (i.e., carboxyl, carbonyl, hydroxyl groups) allowing it to disperse in water and enhancing the electrostatic interactions with cationic dye molecules. GO has attracted tremendous research interests as a promising substrate for the preparation of various graphene-based nanocomposites (Fig. 3).

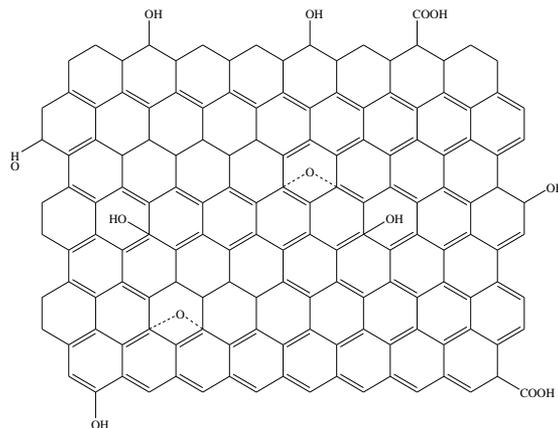


Fig. 3. Schematic representation of the structure of GO.

The good adsorption of GO was found in the removal of MB from aqueous solutions with a maximum absorption capacity of 714 mg/g [147]. The deprotonation of carboxyl groups on GO release H^+ during the adsorption process, which would be neutralized at higher pH, thus the adsorption was favorable.

Table 7. Dyes removal by different nanomaterials.

Adsorbents	Preparation/ modification	Adsorbate	Efficiency	References
Fe_3O_4 nanomaterials	NPs were synthesized by chemical precipitation method using CTAB	Acridine orange	0.056 (mol/g)	[126]
		Coomassie brilliant blue R-250	0.082	
		Congo red	0.078	
HA- Fe_3O_4	Fe_3O_4 NPs were modified by humic acid	Rhodamine B	Adsorption q_{max} -161.8 mg/g (98.5%)	[127]
Fe_3O_4 nanomaterials	Ionic liquid were used to modify Fe_3O_4 nanoparticles	Reactive red 120	166.67 mg/g	[129]
Fe_3O_4 nanomaterials	Polyacrylic-acid bound Fe_3O_4 nanoparticles, which act as core and PAA as ionic exchange	Rhodamine 6G	55.8 mg/g	[130]
Fe_3O_4 nanomaterials	Silica-based - cyclodextrin immobilized on magnetic nanoparticles	Direct blue 15	98%	[131]
MgO nano particles	Co-precipitation method	Reactive black 5	500 mg/g	[138]
MgO nano rods	Artinite and MgO nanorods prepared by precipitation method	Reactive orange	333.34 mg/g	[139]
MgO nanostructures	Hierarchical hydromagnesite and MgO nanostructures prepared by reflux method	Malachite green and Congo red	95.1% and 86.28%	
MgO nanoflakes	Hydro magnesite and MgO nanoflakes prepared by hydrothermal method	Malachite green and Congo red	99.98% and 99.94%	
MgO nano particles	Activated carbon immobilized on MgO nanoparticles	Malachite green and Congo red	97.42%, and 92.68%	
Rice straw charcoal/MgO nanocomposite	Rice straw charcoal immobilized on MgO	Rhodamine B	16.2 mg/g	[140]
GO	-	Reactive blue 221	27.78 mg/g	[141]
		Methylene blue	714 mg/g	[147]
magnetite/reduced graphene oxide	-	Rhodamine B	91%	[143]
nZVI/rGO	-	Malachite green	94%	
		Rhodamine B	87.72 mg/g	[148]

Therefore, it could be found that the increase of removal efficiency lead to the increase of solution pH [143]. Sun *et al.* studied the use of magnetite/reduced graphene oxide nanocomposites (MRGO) to remove Rh B and MG [143]. MRGO nanocomposites exhibit high removal efficiency for Rh B (over 91%) and MG (over 94%). The removal efficiencies of Rh B and MG were still over 80% after five cycles. The performance of MRGO suggested that this can be used effectively for the removal of dye pollutants. The removal of Rh B by reduced graphene oxide-supported nanoscale zero-valent iron (nZVI/rGO) was investigated by Shi and coauthors with the aid of artificial intelligence tools [148]. Response surface methodology (RSM) and artificial neural network hybridized with genetic algorithm (ANN-GA) were used to optimize and predict the optimum conditions and obtain the maximum removal efficiency. The results predicted by the ANN-GA model (90.0%) were compatible with the experimental value (86.4%). The experimental data were fitted well to Freundlich isotherm, and the maximum adsorption capacity based on the Langmuir isotherm was 87.72 mg/g.

Conclusions and future perspectives

The presence of dyes in wastewater is a major concern for environmental conservation and human health. This review has addressed the applications of various dyes removal techniques. The most frequently used dye removal techniques include chemical, physical and biological treatment. The use of chemical methods are restricted due to their high investment and costs. The major disadvantage for application of biological methods is the long hydraulic retention time required for complete decolorization. Adsorption provides high efficiency and low cost for dyes removal. NMs have unique morphological and structural properties that make them particularly attractive for wastewater treatment applications. On the basis of the available literature, it can be concluded that nanomaterials have the potential as desirable adsorbents for removing dyes and the adsorption capabilities of dyes are comparable with or even superior to activated carbon. It seems very plausible that NMs may find wide commercial applications in wastewater treatment in the near future.

Although nanomaterials have presented the ability for the removal of dyes, there are still some issues which need to be addressed. First of all, it is important to investigate the ecotoxicity of nanomaterials in aquatic systems before their widespread applications. Then, additional work should be conducted by the researchers to use NMs in real industrial dye effluents. Thirdly, the processes of regeneration and reuse of NMs are of high interest. Thus, more research work should be focused on the cost-effective and feasible method of the NMs regeneration. In summary, the full-scale study of NMs for removal of dyes from wastewater is required for the practical applicability in future.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under Grants No. 21667012 and 21367009, and the Government of Guizhou Province (Project No. LKS [2013]09).

References

- Petersen, L.; Heynen, M.; Pellicciotti, F., *Freshwater Resources: Past, Present, Future*, **2017**.
- Demirbas, A.; *J. Hazard. Mater.*, **2008**, *157*, 220.
- Arshad, A.; Iqbal, J.; Ahma, I., *Ceram. Int.*, **2017**.
- Kabdasli, I.; Tunay, O.; Orhon, D., *Water Sci. Technol.*, **1996**, *40*, 261.
- Ahmad, A.; Mohd-Setapar, S.H.; Chuong, C.S.; Khatoun, A.; Wani, W.A.; Kumar, R.; Rafatullah, M., *RSC Adv.*, **2015**, *5*, 30801.
- Rajkumar, D.; Jong, G.K., *J. Hazard. Mater. B.*, **2006**, *136*, 203.
- Gómez-Álvarez, A.; Valenzuela-García, J.L.; Meza-Figueroa, D.; O-Villanueva, M.; Ramírez-Hernández, J.; Almendariz-Tapia, J.; Pérez-Segura, E., *Appl. Geochem.*, **2011**, *26*, 2101.
- Anastopoulos, I.; Kyzas, G.Z., *J. Mol. Liq.*, **2014**, *200*, 381.
- Gupta, N., *Artificial neural network; Netw. Complex Syst.*, **2013**, 36.
- Yagub, M.T.; Sen, T.K.; Afroze, S.; Ang, H.M., *Adv. Colloid Interfac. Sci.*, **2014**, *209*, 172.
- Wong, Y.C.; Szeto, Y.S.; Cheung, W.H.; McKay, G., *Process Biochem.*, **2004**, *39*, 695.
- Malik, P. K.; Sanyal, S. K., *Sep. Purif. Technol.*, **2004**, *36*, 167.
- Gupta, V., *J. Environ Manage.*, **2009**, *90*, 2313.
- García-Montaño, J.; Domènech, X.; García-Hortal, J.A.; Torrades, F.; Peral, J., *J. Hazard. Mater.*, **2008**, *154*, 484.
- Hosseini Koupaie, E.; Alavi Moghaddam, M.R.; Hashemi, S. H., *J. Hazard. Mater.*, **2011**, *195*, 147.
- Körbahti, B. K.; Artut, K.; Geçgel, C.; Özer, A., *Chem. Eng. J.*, **2011**, *173*, 677.
- Kant, R., *J. Water Resour. Prot.*, **2012**, *4*, 93.
- Sanmuga Priya, E.; Senthamil Selvan, P., *Arabian J. Chem.*, **2017**, *10*, 3548.
- Grégorio, C.; Pierre-Marie, B., *Prog. Polym. Sci.*, **2008**, *33*, 399.
- Robinson, T.; Chandran, B.; Nigam, P., *Water Res.*, **2002**, *36*, 2824.
- Low, K. S.; Lee, C. K., *Bioresour. Technol.*, **1997**, *61*, 121.
- Annadurai, G.; Juang, R.S.; Lee, D.J., *J. Hazard. Mater.*; **2002**, *92*, 263.
- Foo, K. Y.; Hameed, B. H., *J. Hazard. Mater.*, **2009**, *172*, 523.
- Hameed, B. H., *J. Hazard. Mater.*, **2009**, *161*, 753.
- Mihwa, B.; Ijagbemi, C. O.; Sejin; Dongso, K., *J. Hazard. Mater.*, **2010**, *176*, 820.
- Bello, O. S.; Ahmad, M. A., *International Conference on Environmental Science and Technology (ICEST)*, **2011**, *28*, 505.
- Foo, K. Y.; Hameed, B. H., *Adv. Colloid Interface Sci.*, **2009**, *152*, 39.
- Zawani, Z.; Luqman, C. A.; Choong, T. S. Y., *Equilibrium, Kinetics and Thermodynamic Studies: Adsorption of remazol black 5 on the palm kernel shell activated carbon (PKS-AC)*. *Eur. J. Sci. Res.*, **2009**, *37*, 63.
- Bello, O. S.; Ahmad, M. A., *Sep. Sci. Technol.*, **2012**, *47*, 903.
- Janos, P.; Buchtova, H.; Ryžnarova, M., *Water Res.*, **2003**, *37*, 4938.
- Mohmood, I.; Lopes, C. B.; Lopes, I.; Ahmad, I.; Duarte, A.C.; Pereira, E., *Environ. Sci. Pollut. Res.*, **2013**, *20*, 1239.
- Xu, P.; Zeng, G. M.; Huang, D. L.; Feng, C. L.; Hu, S.; Zhao, M. H.; Lai, C.; Wei, Z.; Huang, C.; Xie, G.X.; Liu, Z.F., *Sci. Total Environ.*, **2012**, *424*, 1.
- Buzzea, C.; Pacheco, I. I.; Robbie, K., *Biointerphases*, **2007**, *2*, 17.
- Wang, S. B.; Sun, H. Q.; Ang, H. M.; Tade, M. O., *Chem. Eng. J.*, **2013**, *226*, 336.
- Fan, M.Y.; Li, T. J.; Hu, J. W.; Cao, R. S.; Wu, Q.; Wei, X. H.; Li, L. Y.; Shi, X. D.; Ruan, W. Q., *Materials*, **2016**, *9*, 687. DOI: 10.3390/ma9080687
- Cao, R. S.; Fan, M. Y.; Hu, J. W.; Ruan, W. Q.; Xiong, K. N.; Wei, X. H., *Materials*, **2017**, *10*, 1279. DOI: 10.3390/ma10111279
- Yuan, Z.; Ahn, S.; Luthy, R. G., *Environ. Sci. Tech.*, **2010**, *44*, 8236.

38. Khin, M. M.; Nair, A. S.; Babu, V. J.; Murugana, R.; Ramakrishna, S., *Energy Environ. Sci.*, **2012**, 5, 8075.
39. Clarke, E.; Anliker, R., *Environ. Chem.* **1980**, 3, 181.
40. Gupta, V., *J. Environ. Manage.*, **2009**, 90, 2313.
41. Hunger, K., *Industrial Dyes-Chemistry, Properties, Application*. Wiley, **2003**.
42. Mishra, G.; Tripathy, M. A., *Colourage*, **1993**, 40, 35.
43. Purkait, M.; DasGupta, S.; De, S., *J. Environ. Manage.*, **2005**, 76, 135.
44. Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A., *J. Hazard. Mater.*; **2010**, 177, 70.
45. Bell, J.; Plumb, J. J.; Buckley, C. A.; Stuckey, D. C., *J. Environ. Eng. Div.*, **2000**, 126, 1026.
46. Saratale, R. G.; Saratale, G. D.; Chang, J. S.; Govindwar, S.P., *J. Taiwan Inst. Chem. Eng.*, **2011**, 42, 138.
47. Soli's, M.; Soli's, A.; Pe'rez, H. I.; Manjarrez, N.; Flores, M., *Process Biochem.*, **2012**, 47, 1723.
48. Wang, H.; Yuan, X.; Zeng, G.; Leng, X.; Liao, K.; Peng, L.; Xiao, Z., *Environ. Sci. Pollut. Res.*, **2014**, 21, 11552.
49. Sen, S. K.; Raut, S.; Bandyopadhyay, P.; Raut, S., *Fungal Biol. Rev.*, **2016**, 30, 112.
50. Aksu, Z.; Karabayur, G., *Bioresour. Technol.* **2008**, 99, 7730.
51. Chung, K. T.; Cerniglia, C. E., *Mut. Res.*, **1992**, 277, 201.
52. Aspland, J. R., Res. Triangle Park, NC, USA, **1997**.
53. Duxbury, D.F., *Chem. Rev.* **2010**, 93, 381.
54. Azmi, W.; Sani, R. K.; Banerjee, U. C., *Enzyme Microb. Technol.*, **1998**, 22, 185.
55. Ghoreishi, S.; Haghghi, R., *Chem. Eng. J.*, **2003**, 95, 163.
56. Kobya, M.; Demirbas, E.; Senturk, E.; Ince, M., *Bioresour. Technol.*, **2005**, 96, 1518.
57. Foo, K. Y.; Hameed, B. H., *Desalin. Water Treat.*; **2010**, 19, 255.
58. Srinivasan, A.; Viraraghavan, T., *J. Environ. Manage.*, **2010**, 91, 1915.
59. McMullan, G.; Meehan, C.; Conneely, A.; Kirby, N.; Robinson, T.; Nigam, P.; Banat, I.M.; Smyth, W.F., *Appl. Microbiol. Biotechnol.* **2001**, 56, 81.
60. Jafaria, N.; Soudib, M.R., *Microbiology*, **2014**, 83, 484.
61. Humnabadkar, R. P.; Saratale, G. D.; Govindwar, S. P., *Asian J. Microbiol. Biotechnol. Environ. Sci.*, **2008**, 10, 693.
62. Tien, M.; Kirk, T.K., *Sci.*, **1983**, 221, 661.
63. Sudha, M.; Saranya, A.; Selvakumar, G. Sivakumar, N., *Int. J. Curr. Microbiol. App. Sci.*, **2014**, 3, 670.
64. Wu, F.; Ozaki, H.; Terashima, Y.; Imada, T.; Ohkouchi, Y.; *Water Sci. Technol.*, **1996**, 34, 69.
65. Levin, L.; Jordan, A.; Forchiassin, F.; Viale, A., *Rev. Argent. Microbiol.*, **2001**, 33, 223.
66. Munari, F.M.; Gaio, T.A.; Calloni, R.; Dillon, A. J. P., *World J. Microbiol. Biotechnol.*, **2008**, 24, 1383.
67. Chang, J. S.; Chen, B. Y.; Lin, Y. S., *Bioresour. Technol.*, **2004**, 91, 243.
68. Stolz, A., *Appl. Microbiol. Biotechnol.*, **2001**, 56, 69.
69. Yang, Q.; Yang, M.; Pritsch, K.; Yediler, A.; Hagn, A.; Schlöter, A.; Kettrup, A., *Biotechnol. Lett.*, **2003**, 25, 709.
70. Meehan, C.; Banat, I.M.; McMullan, G.; Nigam, P.; Smyth, F.; Marchant, R., *Environ. Int.*, **2000**, 26, 75.
71. Kwasniewska, K., *Bull. Environ. Contam. Toxicol.*, **1985**, 34, 323.
72. Horitsu, H.; Takada, M.; Idaka, E.; Tomoyeda, M.; Ogawa, T.; *Eur. J. Appl. Microbiol.*, **1977**, 4, 217.
73. Xiao, X.; Xu, C. C.; Wu, Y. M.; Cai, P. J.; Li, W. W.; Du, D. L.; Yu, H. Q., *Bioresour. Technol.* **2012**, 110, 86.
74. Lin, J.; Zhang, X.; Li, Z.; Lei, L., *Bioresour. Technol.* **2010**, 101, 34.
75. Wang, H.; Zheng, X. W.; Su, J. Q. Tian, Y.; Xiong, X.J.; Zheng, T.L., *J. Hazard. Mater.* **2009**, 171, 654.
76. Chen, H.; Xu, H.; Heinze, T. M.; Cerniglia, C. E., *J. Ind. Microbiol. Biotechnol.* **2009**, 36, 1459.
77. Pearce, C. I.; Christie, R.; Boothman, C.; Canstein, H. V.; Guthrie, J. T.; Lloyd, J. R.; *Biotechnol. Bioengin.*, **2006**, 95, 692.
78. Sanchez-Martin, J.; Beltran-Heredia, J.; Solera-Hernandez, C., *J. Environ. Manage.*, **2010**, 91, 2051.
79. Tatsi, A. A.; Zouboulis, A. I.; Matis, K. A.; Samaras, P., *Chemosphere*, **2003**, 53, 737.
80. Khayet, M.; Zahrim, A. Y.; Hilal, N., *Chem. Eng. J.*, **2011**, 77, 77.
81. Moghammadi, M.; Hassani, A. J.; Mohamed, A. R.; Najafpour, G.D., *J. Chem. Eng. Data*, **2010**, 55, 5777.
82. Man, L. W.; Kumar, P.; Teng, T. T.; Wasewar, K. L., *Desalin. Water Treat.*, **2012**, 40, 260.
83. Turhan, K.; Durukan, I.; Ozturkcan, S. A.; Turgut, Z., *Dyes Pigments*, **2012**, 92, 897.
84. Shaikh, I. A.; Ahmed, F.; Sahito, A. R.; Pathan, A. A., *Pak. J. Anal. Environ. Chem.*, **2014**, 15, 2.
85. Desai, M.; Mehta, M., *Int. J. Eng. Sci. Res. Tech.*, **2014**, 3, 1579.
86. Ezhilkumar, P.; Selvakumar, K. V.; Jenani, R.; Koperun, D. N.; Selvarani, M.; Sivakumar, V. M., *J. Chem. Pharmaceutical Sci.*, **2016**, 9, 259.
87. Seyyedi, K.; Jahromi, M. A. F., *Apcbee Procedia*, **2014**, 10, 115.
88. Marathe, S. D.; Shrivastava, V.S., *Appl. Nanosci.*, **2015**, 5, 229.
89. Veeranna, K. D.; Lakshamaiah, M. T.; Narayan, R. T., *Int. J. Photochemistry*, **2014**, (3).
90. Zaharieva, K. L.; Milenova, K. I.; Cherkezova-Zheleva, Z. P.; Dimova, S. S.; Kunev, B. N.; Eliyas, A. E.; Mitov, I. G.; Stambolova, I. D.; Blaskov, V. N., *Bulg. Chem. Commun.*, **2015**, 47, 342.
91. Mohan, S. V.; Rao, N. C.; Prasad, K. K.; Karthikeyan, J., *Waste Manage.*, **2002**, 22, 575.
92. Do, J. S.; Chen, M. L., *J. Appl. Electrochem.*, **1994**, 24, 785.
93. Louhichi, B.; Ahmadi, M. F.; Bensalah, N.; Gadri, A.; Rodrigo, M.A., *J. Hazard. Mater.*, **2008**, 158, 430.
94. Yang, C. H.; Lee, C. C.; Wen, T. C., *J. Appl. Electrochem.*, **2000**, 30, 1043.
95. Lopes, A.; Martins, S.; Mora'o, A.; Magrinho, M.; Gonc alves, I., *Portugaliae Electrochimica Acta*, **2004**, 22, 279.
96. Crossley, C., *Coloration Technol.*, **2010**, 114, 194.
97. Alventosa-de, Lara, E.; Barredo-Damas, S.; Alcaina-Miranda, M. I.; Iborra-Clar, M. I., *J. Hazard. Mater.*, **2012**, 209, 492.
98. Cheng, S.; Oatley, D. L.; Williams, P. M. Wright, C. J., *Water Res.*, **2012**, 46, 33.
99. Karim, Z.; Mathew, A. P.; Grahn, M.; Mouzon, J.; Oksman, K., *Carbohydr. Polym.*, **2014**, 112, 668.
100. Amin, M. M.; Hafez, A. I.; Shaaban, A. F.; Abdelmonem, N. M.; Hanafy, M., *Membrane*, **2011**.
101. Xu, T. W., *J. Membrane Sci.*, **2005**, 263, 1.
102. Khan, M. I.; Akhtar, S.; Zafar, S.; Shaheen, A.; Khan, M.A.; Luque, R.; Rehman, A., *Materials*, **2015**, 8, 4147.
103. Akazdam, S.; Chafi, M.; Yassine, W.; Gourich, B., *J. Mater. Environ. Sci.*, **2017**, 8, 2993.
104. Dabrowski, A., *Adv. Colloid Interface Sci.*, **2001**, 93, 135.
105. Dawood, S.; Sen, T., *J. Chem. Process Eng.* **2014**, 1, 104.
106. Worth, E., Walter de Gruyter Gmb H & Co. KG, Berlin/Boston. **2012**.
107. Tan, I. A. W.; Ahmad, A. L.; Hameed, B. H., *J. Hazard. Mater.*, **2008**, 154, 337.
108. Hameed, B. H.; Ahmad, A. L.; Latiff, K. N. A., *Dyes Pigments*, **2007**, 75, 143.
109. Satapanajaru, T.; Chompuchan, C.; Suntornchot, P.; Pengthamkeerati, P., *Desalin.* **2011**, 266, 218.
110. Ruan, W. Q.; Shi, X. D.; Hu, J. W.; Hou, Y.; Fan, M. Y.; Cao, R. S.; Wei, X. H., *Appl. Sci.*, **2017**, 8, 3.
111. Weng, C. H.; Lin, Y. T.; Yeh, C. L.; Sharma, Y. C., *Water Sci. Technol.*, **2010**, 62, 844.
112. Gao, C.; Zhang, W.; Li, H.; Lang, L.; Xu, Z., *Cryst. Growth Des.*, **2008**, 8, 3785.
113. Lee, C. K.; Liu, S. S.; Juang, L. C.; Wang, C. C.; Lyu, M. D.; Hung, S. H., *J. Hazard. Mater.*, **2007**, 148, 756.
114. Salehi, R.; Arami, M.; Mahmoodi, N. M.; Bahrami, H.; Khorramfar, S., *Colloids Surf. B*, **2010**, 80, 86.
115. Zhao, Z. S.; Liu, J. F.; Tai, C.; Zhou, Q. F.; Hu, J. T.; Jiang, G. B., *Sci. China Series B*, **2008**, 51, 186.
116. Chang, J. H.; Cheng, S. F., *J. Hazard. Mater.*, **2006**, 131, 153.
117. Kanel, S. R.; Manning, B.; Charlet, L.; Choi, H., *Environ. Sci. Technol.*, **2005**, 39, 1291.
118. Khan, M. S.; Ahmad, A.; Bangash, F. U. K.; Shah, S. S.; Khan, P.; *J. Chem. Soc. Pak.*, **2013**, 35, 744.
119. Rahman, N.; Abedin, Z.; Hossain, M. A., *J. Environ. Sci.*, **2014**, 10, 157.
120. Chatterjee, S.; Lim, S. R.; Woo, S. H., *Chem. Eng. J.*, **2010**, 160, 27.
121. Prema, P.; Thangapandian, S.; Selvarani, M.; Subharanjani, S.; Amutha, C., *Toxicol. Environ. Chem.*, **2011**, 93, 1908.
122. Islam, M. S.; Kusumoto, Y.; Kurawaki, J.; Abdulla-AL-Mamun, M.; Manaka, H., *Bull. Mater. Sci.*, **2012**, 35, 1047.

123. Adekunle, A. S.; Ozoemena, K. I., *Int. J. Electrochem. Sci.*, **2010**, 5, 1972.
124. Afkhami, A.; Saber-Tehrani, M.; Bagheri, H., *Desalin.*, **2010**, 263, 240.
125. Maity, D.; Agrawal, D. C.; *J. Magn. Magn. Mater.*, **2007**, 308, 46.
126. Liang, P.; Qin, P. F.; Lei, M.; Zeng, Q. R.; Song, H. J.; Yang, J.; Shao, J. H.; Liao, B. H.; Gua, J. D., *J. Hazard. Mater.*, **2012**, 209, 193.
127. Chaudhary, G. R.; Saharan, P.; Kumar, A.; Mehta, S. K.; Mor, S.; Umar, A., *J. Nanosci. Nanotechnol.*, **2013**, 13, 3240.
128. Tan, I. A. W.; Ahmad, A. L.; Hameed, B. H., *J. Hazard. Mater.*, **2008**, 154, 337.
129. Absalan, G.; Asadi, M.; Kamran, S.; Sheikhan, L.; Goltz, D. M.; *J. Hazard. Mater.*, **2011**, 192, 476.
130. Zhang, X.; Zhang, P.; Wu, Z.; Zhang, L.; Zeng, G.; Zhou, C., *Colloids Surf. A*, **2013**, 435, 85.
131. Arslan, M.; Sayin, S.; Yilmaz, M., *Water Air Soil Poll.*, **2013**, 224, 1.
132. Nagappa, B.; Chandrappa, G. T., *Micropor. Mesopor. Mater.*, **2007**, 106, 212.
133. Mishakov, I. V.; Bedilo, A. F.; Richards, R. M.; Chesnokov, V. V.; Volodin, A. M.; Zaikovskii, V. I.; Buyanov, R. A.; Klabunde, K. J., *J. Catal.*, **2002**, 206, 40.
134. Richards, R.; Mulukutla, R. S.; Mishakov, I.; Chesnokov, V.; Volodin, A.; Zaikovskii, V.; Sun, N.; Klabunde, K. J., *Scripta Mater.*, **2001**, 44, 1663.
135. Tsuji, H.; Yagi, F.; Hattori, H.; Kita, H., *J. Catal.*, **1994**, 148, 759.
136. Makhluif, S.; Dror, R.; Nitzan, Y.; Abramovich, Y.; Jelinek, R.; Gedanken, A., *Adv. Funct. Mater.*, **2005**, 15, 1708.
137. Stankic, S.; Müller, M.; Diwald, O.; Sterrer, M.; Knözinger, E.; Bernardi, J., *Chem. Int. Ed.*, **2005**, 44, 4917.
138. Jamil, N.; Mehmood, M.; Lateef, A.; Nazir, R.; Ahsan, N., *Adv. Materi.: Tech. Connect Briefs.*, **2015**, 353.
139. Dhal, J. P.; Sethi, M.; Mishra, B. G.; Hota, G., *Mater. Lett.*, **2015**, 141, 267.
140. Daniel, S.; Shoba, U. S., *J. Chem. Pharmaceutical Res.*, **2015**, 7, 713.
141. Moazzam, A.; Jamil, N.; Nadeem, F.; Qadir, A.; Ahsan, N.; Zameer, M., *J. Chem. Soc. Pak.*, **2017**, 39.
142. Sharma, P.; Das, M. R., *J. Chem. Eng. Data*, **2013**, 58, 151.
143. Sun, H.M.; Cao, L.Y.; Lu, L.H., *Nano Res.*, **2011**, 4, 550.
144. Wu, X.L.; Wang, L.; Chen, C.L.; Xu, A. W.; Wang, X. K., *Mater. Chem.*, **2011**, 21, 17353.
145. Su, Q.; Pang, S.; Alijani, V.; Li, C.; Feng, X.; Mullen, K., *Adv. Mater.*, **2009**, 21, 3191.
146. Liu, K. P.; Li, H. M.; Wang, Y. M.; Gou, X. J.; Duan, Y. X., *Colloids and Surf. A: Physicochem. Eng. Aspects*, **2015**, 477, 35.
147. Yang, S. T.; Chen, S.; Chang, Y. L.; Cao, A.; Liu, Y. F.; Wang, H. F., *J. Colloid Interface Sci.*, **2011**, 359, 24.
148. Shi, X. D.; Ruan, W.Q.; Hu, J. W.; Fan, M. Y.; Cao, R. S.; Wei, X. H., *Nanomaterials*, **2017**, 7, 309.

DOI: 10.3390/nano7060134