

A comparative study on the basis of adsorption capacity between CNTs and activated carbon as adsorbents for removal of noxious synthetic dyes: a review

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Abstract Rapid removal of noxious synthetic dyes from wastewater is of great concern in the scientific research field, this is due to the expansion of harmful effects of synthetic dyes traces in water streams on the environment and human health with the exponential rise in concentration of synthetic dye globally and demand in various industries that coincided with the implantation of more stringent water quality standards. Various technologies have been applied for the removal of synthetic dye from wastewater, including adsorption technology, which has a great potential in treating varieties of synthetic dyes. This article comprehensively reviews the latest progress in the development of carbon nanotubes (CNTs) and their applications for the removal of synthetic dyes from

wastewater, including functionalized of CNTs and their researched counterparts. The emerging trends in the development of alternative adsorbents with different substrates, morphologies, and functional groups are also elucidated.

Keywords Carbon nanotubes (CNTs) · Activated carbon (AC) · Synthetic dyes · Adsorption · Functionalization · Wastewater treatment

Abbreviations

AB161	Acid blue 161
AC	Activated carbon
AR18	Acid red 18

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AR183	Acid red 183
ARS	Alizarin red S
BR	Bromopyrogallol red
BR46	Basic red 46
BTB	Bromothymol blue
Cd	Cadmium hydroxide nanowire-loaded
(OH) ₂ -NW-AC	activated carbon
CNF	Carbon nanofibers
CNTs	Carbon nanotubes
CR	Congo red
CSBs	CNT-impregnated chitosan hydrogel beads
DMBAR	5-(4-dimethyl benzylidene amino) Rhodanine
HCNTs	Hybrid CNTs
MB	Methyl blue
MG	Methyl green
MO	Methyl orange
MR	Methyl red
MWCNTs	Multi-walled carbon nanotubes
OII	Orange II
PAC	Powdered activated carbon
PAHs	Poly-aromatic hydrocarbons
RB29	Reactive blue 29
RB4	Reactive blue 4
RR120	Reactive red 120
RRM	Reactive red M-2BE
SDS	Sodium dodecyl sulfate
SO	Safranin O
SWCNTs	Single-walled carbon nanotubes
TB	Toluidine blue

Introduction

The application of carbon nanomaterials such as carbon nanotubes (CNTs) in the field of adsorption is one of the emerging trends for the removal of dyes from wastewater,

even at very low concentrations [1]. CNTs can be visualized as graphitic carbon sheets rolled into hollow cylinders with nanometer-scale diameters and micrometer-scale lengths [2, 3]. Owing to their unique properties, the production and chemical variations of CNTs has been growing rapidly [4]. These chemical variations are created by the unique bonding configurations of carbon that make it a ubiquitous part of our environment. The one-dimensional nature of the basic CNT structure enables ultra-high surface area, the ability to act as a semiconductor or a metal, the existence of multiple direct band gaps, the relative ease of attachment for numerous chemical functional groups, and the ability to decorate CNTs with nanoparticles [4–7].

In this review, we highlight the past and present attempts for using CNTs as adsorbents for the removal of synthetic dyes. Furthermore, the effect of surface modification of CNTs by synthetic dyes is in the core of this review.

Synthetic dyes

The major structure element responsible for light absorption in dye molecules is the chromosphere group, i.e., a delocalized electron system with conjugated double bonds. Usually chromospheres contain heteroatoms such as N, O, and S, with non-bonding electrons. Common classes of dyes, based on the chromosphere present, are shown in Table 1 [8–11]. Dyes were also usually classified based on their particle charge upon dissolution in aqueous application medium [12, 13], to cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) as shown in Table 2 [14, 15].

Carbon nanotubes (CNTs)

The discovery of carbon nanotubes in 1991 by Iijima [16] brought revolutionary changes into the field of nano-adsorbents during the last decade that showed a boom as evidenced from the huge number of literature. Carbon nanotubes are basically rolled up graphene sheets (hexagonal structures) into cylindrical form and capped with half shape of fullerene structure [5]. There are two types of carbon nanotubes (Fig. 1): (a) single-walled carbon nanotubes (SWCNTs), that can be considered as a single graphene sheet rolled into a cylinder and (b) multi-walled carbon nanotubes (MWCNTs), which can be considered as stacking of concentric layers of several graphene sheets in the form of cylinders with an interspacing of 0.34 nm. Based on the atomic arrangement there are three types of structures: (1) zigzag, (2) armchair and (3) chiral structures (Fig. 2) [5, 17]. The properties of carbon nanotubes are

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Table 1 Synthetic dye structures according to their chromophores adapted from [8–11]

Class	Chromophore	Example
Nitro		
Nitroso		
Azo		
Triphenylmethane		
Phthalein		
Indigo		
Anthraquinone		

highly dependent on morphology, size and diameter [3]. Carbon nanotubes can be metallic or semiconducting depending on the atomic arrangement of carbon nanotubes. Initially, MWCNTs were prepared by Iijima using arc evaporation method in 1991 [16–18]. Later on, the same researcher reported the discovery of SWCNT in 1993 prepared by arc evaporation of metal impregnated (Fe-graphite) electrodes in the presence of methane-argon [18, 19].

In addition to the pioneer study of Iijima for the preparation of MWCNTs and SWCNT using arc evaporation method [16–19], other methods have been reported including laser ablation [19], chemical vapor deposition [20], electrolysis [20], flame synthesis [19], etc. It is worth mentioning that arc evaporation method, laser ablation and chemical vapor deposition are the most common techniques which are used broadly for synthesis of CNTs [20, 21].

The adsorptive surface of the CNTs by nature is highly hydrophobic [21]. To overcome this problem in raw CNTs, different methods of surface modification have been pursued using non-covalent [22] and covalent functionalization [23] strategies.

CNTs surface modifications have been conventionally classified mainly into three categories depending on the method for achieving modification [24, 25]: (1) mechanical, (2) physicochemical, and (3) irradiation. Physicochemical methods had been most widely adopted, namely, covalent surface modification and non-covalent surface modification, depending on whether or not covalent bonding between the CNTs and the functional groups and/or modifier molecules is involved in the surface modification process [24–27].

Non-covalent functionalization strategies do not have any effect on the physical properties of the CNTs because they keep the structure of intrinsic sp^2 hybridized orbital unchanged. This can be done by taking advantage of the π - π interaction between conjugated molecules and the graphitic sidewall of CNTs [24–26]. Other methods such as non-covalent hydrophobic interactions (amphiphilic molecules) with aromatic surface of CNTs in aqueous media have also been explored, which can reduce the hydrophobic interface between the CNTs and their polar environment [27–33].

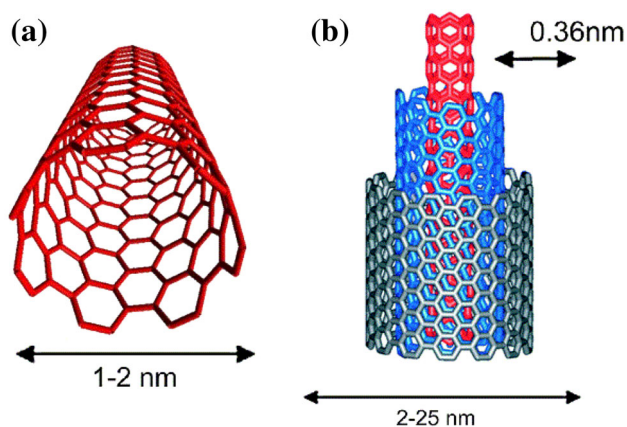
Covalent functionalization depends on the chemical reaction between the carbon atoms of CNTs and conjugation of hydrophilic organic molecules on the surface of CNTs. The ‘ends and defects’ and ‘side walls’ functionalizations are the two subcategories of covalent functionalization, whereas the former one is more specific and reactive than the later [28–34].

The chemical treatment of pristine CNTs with most widely used strong oxidative agents (concentrated H_2SO_4 and HNO_3 with molar ratio 3:1) generate the oxygenated groups such as carboxylic, ketone, alcohol, and ester at ‘ends and defects’ sites of CNTs. This treatment not only generates the various functional groups, but also cut and shortens the CNTs into the smaller pieces. Side wall functionalization introduces higher concentration of covalently attached functional groups on the CNTs surface with the trade-off of significant perturbation in the electronic structure [35–38]. A more detailed account about the recent progress in the chemical modifications of CNTs was reviewed by Karousis et al. [39]. In this review, we summarized the different functionalization schemes of CNTs in Fig. 3. This shows that different functionalities have added on CNT surfaces through different routes. Such treatments increase the affinity of CNT towards wastewater pollutants, which are subsequently trapped into the nanotube’s surface [17].



Table 2 Classification of dyes based on their chemical nature adapted from [14, 15]

Class	Substrate	Method of application	Chemical types
Acid dyes	Wool, nylon, silk, inks, leather and paper	Generally from neutral to acidic bath	Anthraquinone, xanthene, azo, nitro, and triphenylmethane
Basic dyes	Inks, paper, polyacrylonitrile, treated nylon, and polyester	Applied from acidic dye baths	Hemicyanine, azo, cyanine, diazahemicyanine, azine, diphenylmethane, xanthene, triarylmethane, acridine, anthraquinone and oxazine
Direct dyes	Nylon, rayon, paper, leather and cotton	Applied from neutral or a little alkaline bath containing additional electrolyte	Phthalocyanine, azo, oxazine, and stilbene
Disperse dyes	Polyamide, acrylic polyester, acetate, and plastics	Fine aqueous dispersions often applied by high-temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and thermo fixed	Benzodifuranone, azo, anthraquinone, nitro, and styryl
Reactive dyes	Wool, cotton, silk and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH	Anthraquinone, formazan, phthalocyanine, azo, oxazine and basic
Sulphur dyes	Rayon and cotton	Aromatic substrate vatted with sodium sulphide and reoxidized to insoluble sulphur-containing products on fiber	Indeterminate structures
Vat dyes	Wool and cotton	Water-insoluble dyes solubilized by dropping in sodium hydrogen sulphite, then exhausted on reoxidized and fiber	Indigoids and anthraquinone

**Fig. 1** Schematics of a SWCNTs (a) and MWCNTs (b)

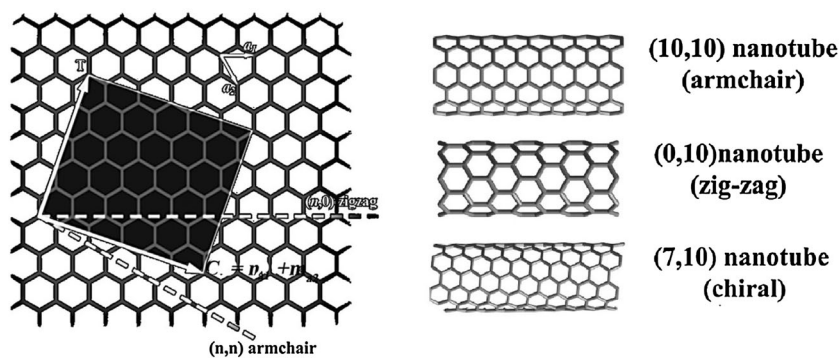
Treatment with different acidic and oxidizing agents on CNTs leads to different surface area and adsorption capacity. Some of them are listed in Table 3 with corresponding surface area and adsorption capacities [40]. In addition, functionalities can increase the solubility of CNTs and bring CNTs to repulse each other, which help free movement of individual CNT in homogeneous solution without aggregation. Aggregation can decrease the affinity of interactions between synthetic dyes and nanotube surfaces [17].

Adsorption of synthetic dyes on CNTs and a comparison with activated carbon (AC)

Adsorption is commonly employed as a polishing step to remove synthetic dyes contaminants in wastewater treatment. Efficiency of conventional adsorbents is usually limited by the surface area or active sites, the lack of selectivity, and the adsorption kinetics [41]. CNT adsorbents offer significant improvement with their extremely high specific surface area and associated sorption sites, short intraparticle diffusion distance, and tunable pore size and surface chemistry [42]. In addition, CNTs can be considered as one of the most promising adsorbents for this purpose because of their large adsorption capacity for synthetic dyes [5]. Indeed, MWCNTs have been shown to outperform cadmium hydroxide nanowire-loaded AC ($\text{Cd}(\text{OH})_2\text{-NW-AC}$) with respect to their efficient removal of safranin O (SO) from wastewater [43]. However, only a few studies on the application of CNTs for dye removal from aqueous solution have been reported [44–49] and the CNTs were typically directly used without further treatment [45–47, 49] (Table 4).

Functionalization of CNTs has been undertaken because the introduction of various functional groups can provide new adsorption sites for synthetic dyes. Among such modifications, oxidation is an easy method of introducing

Fig. 2 Molecular models of exhibited by SWNTs based on the chirality



hydroxyl and carbonyl groups to the sidewalls of CNTs. Oxidized MWCNTs have been shown to be effective in the removal of methyl red (MR) [50] and methylene blue (MB) from aqueous solutions [51].

Mahmoodian et al. [52] studied the adsorption of methyl orange (MO) onto pHEMA–CS–f-MWCNT and reported an adsorption capacity of 306 mg g^{-1} for removal of MO onto CNTs. Shahryari et al. [53] performed the same batch of experiments on MWCNTs having a higher surface area of $280 \text{ m}^2/\text{g}$ as compared to that of CNTs used by Mahmoodian et al. and reported a higher methyl blue (MB) adsorption of 132.6 mg g^{-1} at 310 K. We suggest that the adsorption capacity also depends on the experimental conditions and nature and type of the adsorbent. In ref. [53] the authors used MWCNTs as adsorbent while ref. [52] reported the use of CNTs.

Rodríguez et al. [54] compared the adsorption capacity of cationic MB and anionic orange II (OII) from aqueous solution by using MWNTs and carbon nanofibers (CNF) as adsorbents. The adsorption of MB onto CNF was slightly higher than adsorption onto MWCNTs, while for OII the adsorption capacity of CNF was $(66.12 \pm 2.11) \text{ mg g}^{-1}$ and MWCNTs was $77.83 \pm 1.6 \text{ mg g}^{-1}$.

In another study, the reverse adsorption capacity was observed for the removal of Reactive Red M-2BE (RRM) onto MWCNTs and powdered activated carbon (PAC) while PAC had a higher surface area of $728.7 \text{ m}^2/\text{g}$ than that of MWCNTs ($180.9 \text{ m}^2/\text{g}$) [55]. The maximum amounts of RRM uptake were 335.7 and 260.7 mg g^{-1} for MWCNT and PAC, respectively. Accordingly, we can justify the higher adsorption capacity on the basis of the higher average pore diameter of MWCNTs which was 7.62 nm as compared to 3.52 nm for PAC. Due to the larger pore size, the dyes molecules can easily be diffused from surface though the pores of MWCNTs.

The development of CNT-impregnated chitosan hydrogel beads (CSBs) for the removal of Congo red (CR) has been investigated [56, 57]. In Langmuir adsorption modeling, CSBs demonstrated a higher maximum adsorption capacity than normal chitosan CBs (450.4 vs. 200.0 mg g^{-1}) [56]. A new generation of CSBs prepared by using sodium dodecyl sulfate (SDS) and MWCNTs to improve their mechanical

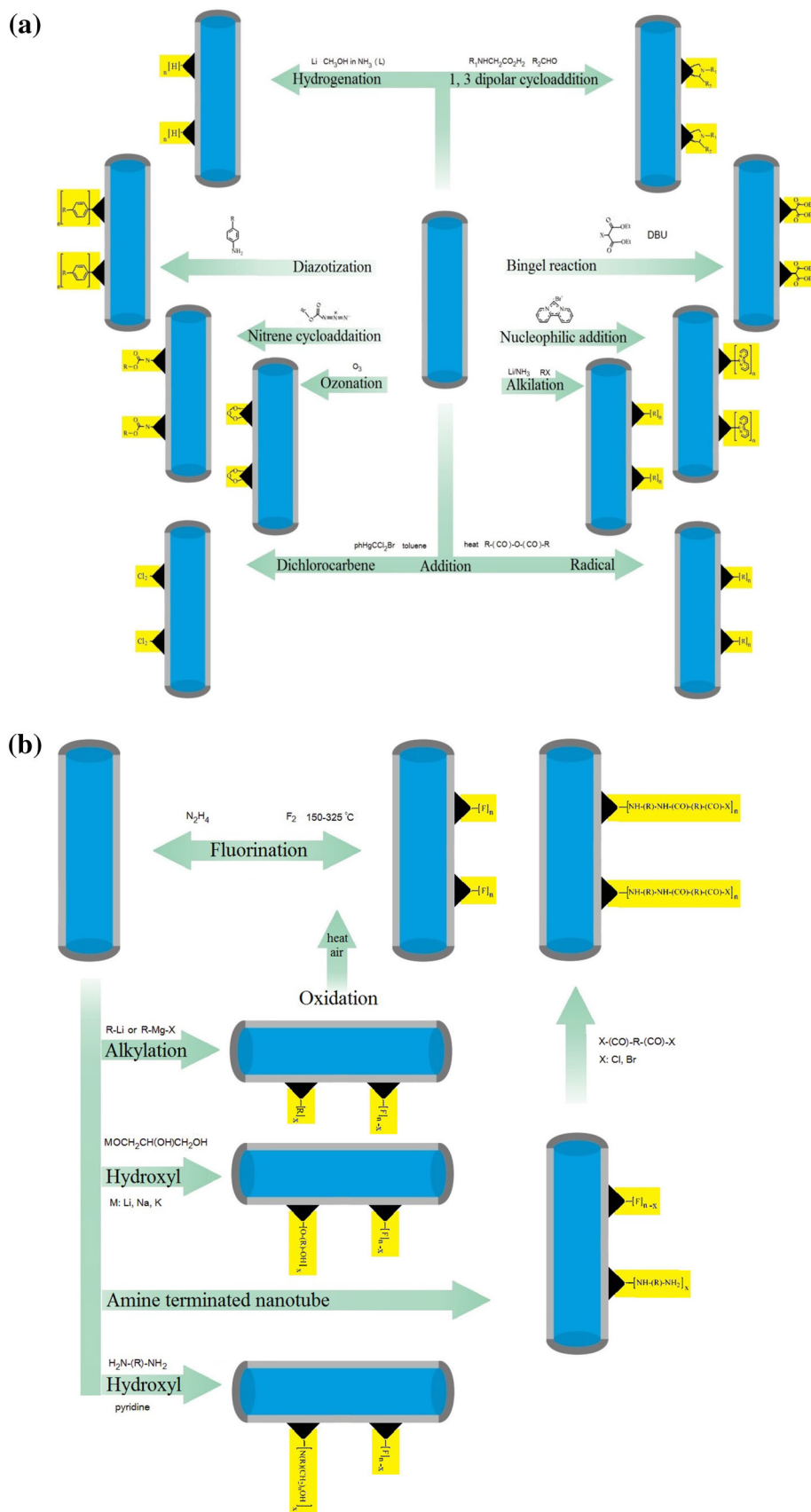
properties has demonstrated a high maximum adsorption capacity for CR (375.94 mg g^{-1}) [57]. Compared to MWCNTs and hybrid CNTs (HCNTs), SWCNTs can demonstrate better adsorption properties for organic contaminants because of their higher specific surface area [41]. Indeed, SWCNTs are more efficient for the removal of benzene and toluene, and has shown maximum adsorption capacities of 9.98 and 9.96 mg g^{-1} , respectively [58]. A maximum adsorption capacity of 496 mg g^{-1} was achieved when reactive blue 29 (RB29) was removed from aqueous solution using SWCNTs [59, 60].

CNTs have shown higher efficiency than AC on adsorption of various synthetic dyes [73]. The high adsorption capacity mainly stems from the large specific surface area and the diverse contaminant–CNT interactions. The available surface area for adsorption on individual CNTs is their external surfaces [74]. In the aqueous phase, CNTs form loose bundles/aggregates due to the hydrophobicity of their graphitic surface, reducing the effective surface area [73–75]. On the other hand, CNT aggregates contain interstitial spaces and grooves, which are high adsorption energy sites for organic molecules [75]. Although activated carbon possesses comparable measured specific surface area as CNT bundles, it contains a significant number of microspores inaccessible to bulky organic molecules such as many antibiotics and pharmaceuticals [76]. Thus CNTs have much higher adsorption capacity for some bulky organic molecules because of their larger pores in bundles and more accessible sorption sites.

A major drawback of AC is its low adsorption affinity for low molecular weight polar organic compounds. CNTs strongly adsorb many of these polar organic compounds due to the diverse contaminant–CNT interactions including hydrophobic effect, π – π interactions, hydrogen bonding, covalent bonding, and electrostatic interactions [74]. The π electron-rich CNT surface allows π – π interactions with organic molecules with C=C bonds or benzene rings, such as poly-aromatic hydrocarbons (PAHs) and polar aromatic compounds [77, 78]. Organic compounds which have –COOH, –OH, –NH₂ functional groups could also form hydrogen bond with the graphitic CNT surface which



Fig. 3 Surface functionalization of CNTs through different routes: normal methods (a), other related methods (b)



donates electrons [79, 80]. Electrostatic attraction facilitates the adsorption of positively charged organic chemicals such as some antibiotics at suitable pH [76].

Table 3 Adsorption capacities and surface area of CNTs [40]

CNTs (m ² /g)	Adsorption capacity (mg/g)	Surface area
Pristine CNTs	1.10	82.20
H ₂ O ₂ oxidized	2.60	130.0
HNO ₃ oxidized	5.10	84.30
KMnO ₄ oxidized	11.00	128.0

Table 4 Removal of synthetic dyes using CNTs

CNTs	Modification method	Dye adsorbed	Adsorption effect (mg g ⁻¹)	References
SWCNTs	Pristine	BR46	38.35	[41]
SWCNTs	Oxidized	BR46	49.45	[41]
MWCNTs	Refluxed pristine MWCNTs in concentrated HNO ₃ /H ₂ SO ₄ mixture for 4 h	TB, MB, MG, BR	Not provided	[44]
MWCNTs	Untreated	ARS	161.290	[45]
MWCNTs	Untreated	morin	26.247	[45]
MWCNTs	Untreated	ECR	73.18	[46]
MWCNTs	Untreated	Arsenazo(III)	Not provided	[47]
MWCNTs	Oxidized using concentrated nitric acid	MO	Not provided	[48]
MWCNTs	Untreated	RRM	335.7	[49]
MWCNTs	Oxidized	MR	108.7	[50]
MWCNTs	Oxidized	BTB	55.3	[51]
MWCNTs	Oxidized and microwave method	MO	306	[52]
MWCNTs	Untreated	MB	132.6	[53]
MWCNTs	Untreated	MB	77.83 ± 1.6	[54]
MWCNTs	Untreated	RRM	335.7	[55]
MWCNTs	CNT-impregnated chitosan hydrogel beads (CSBs)	CR	450.4	[56]
MWCNTs	CSBs prepared by using sodium dodecyl sulfate (SDS)	CR	375.94	[57]
SWCNTs	Untreated	RB29	496	[59]
MWCNTs	Untreated	CR	Not provided	[61]
MWCNTs	Untreated	MO	Not provided	[62]
MWCNTs	Alkali-activated	MB	399	[63]
MWCNTs	Alkali-activated	MO	149	[63]
MWCNTs	Untreated	AR18	166.67	[64]
MWCNTs	Untreated	MB	59.7	[65]
MWCNTs	Untreated	AR183	5.2	[65]
MWCNTs	Untreated	AB 161	91.68 %	[66]
MWCNTs	Untreated	RB4	69	[67]
MWCNTs	Untreated	AR183	45	[67]
MWCNTs	Fabricated magnetic MWCNTs by Fenton's reagent method (M-MWCNTs)	MO	28	[68]
MWCNTs	Oxidized	DMBAR	15.52	[69]
MWCNTs	Produced by Ni nanoparticle catalyzed pyrolysis of methane in a hydrogen and nitrogen flow at 650 °C	MB	188.68	[70]
MWCNTs	Untreated	Triclosan	153.1	[71]
SWCNTs	Untreated	RR120	426.49	[72]

Conclusion

This article reviews the different adsorption technique using CNTs used for the removal of synthetic dyes from wastewaters. Many reports confirmed that CNTs have higher efficiency than AC on the adsorption of various synthetic dyes. A wide range of CNT-based adsorbents obtained from surface modification of CNTs has been investigated. Several researchers demonstrated that the surface modification of CNTs has a high impact on improving their performance and ability to adsorb synthetic dyes from aqueous solutions. It has also been demonstrated that



surface modification of CNTs, in general, improves the adsorption capacity of adsorbents probably due to the increased number of active binding sites resulting from surface modification and formation of new functional groups that favors the adsorption of synthetic dyes. Although surface modification of CNTs can enhance the adsorption of synthetic dyes, the cost of chemicals used and methods of modification also have to be taken into consideration. As far as the modification of an adsorbent surface might change the overall properties of the adsorbent, characterization studies involving surface area pore size, porosity are recommended for any future work on surface modification of CNTs.

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