

A review on Carbon nanotubes adsorbents for the removal of pollutants from aqueous solutions

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ABSTRACT: Carbon nanotubes (CNTs) are a novel material that exhibits good adsorption behavior toward various toxic pollutants in aqueous solution. These adsorbents have a fast adsorption rate and high adsorption efficiency, efficient to remove various pollutants and they are easy to recover and reuse. These features highlight the suitability of CNTs for the treatment of water polluted with heavy metal ions and dyes. This review outlines the preparation of CNTs as well as different methods of surface modification of these materials by non-covalent and covalent functionalization strategies. Additionally, an overview of recent developments and applications of CNTs for heavy metal ions and dyes pollutant removal is discussed in detail. Based on current research and existing materials, some new and futuristic approaches in this fascinating area are also discussed. The main objective of this review is to provide up-to-date information about the most important features of CNTs and to show their advantages as adsorbents in the treatment of polluted aqueous solutions.

Keywords: Adsorption; Carbon nanotubes; Dyes; Heavy metal ions; Pollutant; Removal

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INTRODUCTION

Besides in the rapid growth of the world population, industrialization, unplanned urbanization, agricultural activities as well as the excessive use of chemicals have contributed to environmental pollution. Nowadays, the discharge of chemicals into the environment is a serious problem affecting both water and soil quality. When present in discharge, trace pollutants are released into the environment in forms that are easily assimilated by fauna and flora. They can then accumulate in organisms, undergoing bio-magnification through the food webs. Many pollutants exert toxic effects not only on the

environment but also on humans. Thus, a constant effort to protect water resources is being made by the various governments, through the introduction of increasingly strict legislation [1,2].

The most common toxic ions in aqueous solutions responsible for particular problems were heavy metal ions, dyes, etc. [3-5]. Despite of the fact that the human body needs small dose such as Zn^{2+} , an excess of it may cause eminent health problems such as depression, lethargy, neurological signs and increased thirst. Exposure to such toxic ions can cause health problems such as liver or kidney damage, Wilson disease, insomnia, cancer, diarrhea, nausea, vomiting, dermatitis, chronic asthma, coughing and headache [6-11].

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Removal of these toxic ions from wastewater is necessary for many health and environmental considerations. Conventional methods such as reduction, precipitation, adsorption, oxidation and ion exchange have been used to remove these ions. However, adsorption process was the most suitable method because of its high efficiency and economic consideration [12-14]. Some adsorbents such as activated carbon, zeolites, biomaterials, nanoparticles, polymers, etc., have been extensively used for adsorption [13-25]. However, the adsorption efficiency of these adsorbents was very low. Therefore, it has become the center of attention of different research groups to find more efficient adsorbents.

Since the discovery of Carbon Nanotubes (CNTs) [26], it has become the favorite adsorbent among carbon nanomaterials because of their unique physical and chemical properties [27-31]. Note that there are two main types of CNTs: single-walled (SWCNTs) and multi-walled (MWCNTs). In the last decade, CNTs have found a great potential application for removing heavy metal ions and dyes [32-46]. In this review, we highlight the past and present attempts at using CNTs as adsorbents to removing heavy metal ions and dyes.

Application of CNTs in the removal of pollutants

Preparing of adsorbent

CNTs surfaces are by nature highly hydrophobic. To overcome this problem in raw CNTs, different methods of surface modification are being pursued by non-covalent and covalent functionalization strategies [47].

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 orbitals unchanged. This can be done by taking advantage of the π - π interaction between conjugated molecules and the graphitic sidewall of CNTs [48-50].

Another method such as non-covalent hydrophobic interactions (amphiphilic molecules) with aromatic surface of CNTs in aqueous media has been explored, which can reduce the hydrophobic interface between the CNTs and their polar environment [51-59]. Functionalization in covalent method depends on the chemical bonds between carbon atoms of CNTs, chemical reactions and conjugation of hydrophilic organic molecules on the surface of CNTs [28].

According to the location of the functional groups, the strategies to covalently functionalize CNTs can be classified into two main categories: defect functionalization and sidewall functionalization. The covalent functionalization of CNTs is more robust and better controllable compared to functionalization based on non-covalent methods [60-65].

The defect functionalization of CNTs is based on the conversion of carboxylic groups and other oxygenated sites formed through oxidative purification. The carboxylic groups at the end of the CNTs can be coupled with other functional groups. The oxidized CNTs usually react with thionyl chloride to activate the carboxylic group for a later reaction with amines or alcohols [66-70].

The sidewall functionalization is based on covalent linkage of functional groups onto the sidewall of CNTs. The covalent sidewall functionalization is associated with the change of hybridization from sp^2 to sp^3 and a simultaneous loss of conjugation.

In contrast to the well-developed chemistry of fullerenes, the covalent functionalization chemistry of CNTs has only been achieved recently [71]. This might be either related to the lack of availability of SWCNTs in the 1990s or to the significantly lower reactivity of the commercially available CNTs [72] compared to fullerenes. Not surprisingly, most of the reported sidewall functionalization reactions of CNTs require very reactive reagents. Nevertheless, within the last few years a diverse chemistry was developed to covalently modify the surface of CNTs [73].

The pioneer study on covalent sidewall functionalization of CNTs was achieved by Mickelson *et al.* in 1998, through the treatment of CNTs with elemental fluorine [66]. The degree of addition ranges from 0.1% to the complete combustion of the CNTs under these drastic conditions. Subsequent treatment of the fluoro-nanotubes with N_2H_4 or $LiBH_4/LiAlH_4$ leads to the restoration of the CNTs [108]. Fluorinated CNTs are now commercially available and therefore, give rise to a widespread chemistry by using them as starting material to carry out subsequent derivatization reactions. Thus, sidewall-alkylation of the nanotubes was achieved by the nucleophilic substitution with Grignard-reagents or the reaction with alkyllithium precursors [74]. Oxidation in air or heat treatment leads to the removal of the alkyl groups and therefore the functionalization of the SWCNTs. Electrochemical addition of aryl radicals

to the CNTs has also been reported by Bahr *et al.* [75]. The addition of radicals on CNTs was first introduced by Holzinger *et al.* who used heptadecafluorooctyl iodide to photoinduce the generation of the perfluorinated radicals followed by their addition to the SWCNTs [67]. Other studies used organic peroxides as precursors to achieve covalent sidewall functionalization [76]. Chen *et al.* reported the addition of carbenes by the reaction of SWCNTs with dichlorocarbene [77]. The carbene was first generated from chloroform with potassium hydroxide [68], and later from phenyl (bromodichloromethyl) mercury [78]. The addition of nucleophilic carbenes on the electrophilic SWCNTs resulted in the formation of a zwitterionic poly adduct [67]. The covalently bound imidazolidene addend bears a positive charge whereas, the nanotube bears one negative charge for each addend attached to the sidewall causing the n-doping of the CNTs [79]. This offered a new approach for the controlled modification of the electronic properties of SWCNTs. The addition of nitrenes on the sidewall of CNTs was achieved via reactive alkyl oxycarbonyl nitrenes obtained from alkoxycarbonyl azides [80, 81]. Prato *et al.* succeeded in the development of one of the most powerful techniques for the functionalization of CNTs using the 1,3-dipolar cycloaddition of azomethine ylides [82]. The treatment of pristine SWCNTs with an aldehyde and an N-substituted glycine derivative resulted in the formation of substituted pyrrolidine moieties on the SWCNT surface [83].

Removal of heavy metal ions

Zinc is one of the most common heavy metals occurring in wastewater. In water, Zn ion may associate or react with neutral or ionic compounds to form inorganic salts, stable organic complexes or inorganic or organic colloids. The quantity of Zn ion available in water from each of these forms is dependent upon the solubility of these forms, the pH and temperature, the total amount of the Zn form present in water and the presence of other metal ions, organic compounds and inorganic compounds. Zn ion exhibits high toxicity to aquatic organisms and it may cause high chronic toxicity in some cases. For example, Zn ion is highly toxic to aquatic organisms and has a high potential to bio-accumulate. Therefore, it is important to remove Zn from wastewater during the treatment. Lu and Chiu [84] in their study explained the trend of the graph

obtained from the adsorption capacity of Zn^{2+} onto the CNTs, where adsorption increased when the pH is adjusted from 1-8, achieved maximum between pH 8-11 and decreased at pH 12. The time taken for the adsorption to reach the equilibrium for the SWCNTs and MWCNTs are 1 hour, while for the powdered activated carbon (PAC) it took twice that long or 2 hours.

A comparison on the adsorption of Zn^{2+} between the CNTs and commercial PAC was also carried out. With the initial Zn^{2+} concentration range of 10-80 mg L^{-1} , the maximum adsorption capacities of Zn^{2+} calculated by the Langmuir model for the SWCNTs, MWCNTs and PAC were 43.66, 32.68 and 13.04 mg g^{-1} , respectively. The time taken to reach equilibrium was short and they suggested that in order to obtain high adsorption capacity, SWCNTs and MWCNTs are preferably used for Zn^{2+} removal from water. In another case study, Lu *et al.* [85] reported that the amount of Zn^{2+} sorbed onto the CNTs increased with a rise in temperature. Using the same conditions, the Zn^{2+} sorption capacity of the CNTs was much greater than that of the commercially available PAC, reflecting that the SWCNTs and MWCNTs are effective sorbents. The thermodynamic analysis revealed that the sorption of Zn^{2+} onto the CNTs is endothermic and spontaneous. The Zn^{2+} ions could be easily removed from the surface site of the SWCNTs and MWCNTs by a 0.1 mol/L nitric acid solution and the sorption capacity was maintained after 10 cycles of the sorption/desorption process. This suggests that both CNTs can be reused through many cycles of water treatment and regeneration.

Not only the Zn ions could be removed by the CNTs adsorption, other studies show that some other trace elements such as Ni, Pb, Cd, Cr and Cu can also be absorbed by this powerful CNT agent.

Yang *et al.* [86], in their study on adsorption of Ni^{2+} on oxidized MWCNTs, found that the CNT adsorption capacity increases with the increase of pH in the pH range of 2-9 from zero to ~99%. They found that oxidized MWCNTs were the most suitable material for the solidification and pre-concentration of Ni^{2+} from aqueous solutions. In another article, Kandah and Meunier [87], reported on their achievement in adsorption of some heavy metals using functionalized CNTs. With a large adsorption capacity, they also reported on the ability of the CNTs to remove some organic dyes from water. In their study, for both

produced and oxidized CNTs, the Langmuir model determined 18.08 and 49.26 mg/g, respectively, as the maximum Ni²⁺ adsorption uptake. These two sets of isotherm models fit well with the experimental data. Therefore we conclude that the experiment was successful where the CNTs were found to be the most effective nickel ion absorbent based on the high adsorption capacity as well as the short adsorption time [88].

Chromium at low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damages as well as damaging the circulatory and nerve tissues. Once again, it is important to eliminate such traces in our wastewater by the aid of the CNTs. Atieh [89] has reported using carbon nanotubes supported by activated carbon (AC) to remove Cr⁶⁺ ions from polluted water. The highest adsorption capacity by using AC-CNT coated adsorbent obtained from batch adsorption experiments was 9.0 mg/g. Therefore, it seems that AC coated with CNTs is most effective for the removal of chromium ions. Di *et al.* [90] reported the removal of Cr⁶⁺ from drinking water using ceria nanoparticles supported on aligned carbon nanotubes (CeO₂/ACNTs).

The largest adsorption capacity of CeO₂/ACNTs reaches 30.2 mg g⁻¹ at an equilibrium Cr⁶⁺ concentration of 35.3 mg l at pH 7.0. They also concluded that the adsorption capacity of the CeO₂/ACNTs is 1.5 times higher than that of the AC, 2.0 times higher than that of Al₂O₃ and 1.8 times higher than that of ball-milled ACNTs. The high adsorption capacity and the wide range of pH values make CeO₂/ACNTs a good candidate material for removal of Cr⁶⁺ from drinking water. Hu *et al.* [91] reported the removal of Cr⁶⁺ from aqueous solution using oxidized MWCNTs. The maximum removal of Cr⁶⁺ was found at low pH, and the adsorption kinetics of Cr⁶⁺ was suitable for pseudo-second-order models. The removal of chromium mainly depends on the occurrence of redox reaction of adsorbed Cr⁶⁺ on the surface of oxidized MWCNTs to the formation of Cr³⁺ and subsequent sorption of Cr³⁺ on MWCNTs. This Cr³⁺ sorption appears to be the leading mechanism for chromium uptake to MWCNTs. To remove the anionic chromate (CrO₄²⁻) from wastewater, functionalized CNTs were found to be the most suitable compared to unmodified CNTs in terms of the adsorption capacity [92]. The authors explained the reason for the CNTs showing excellent adsorption

capability of anionic chromate, because of the interaction of CrO₄²⁻ with the surface oxygen-containing functional groups on the modified CNTs. Hence, functionalized CNTs once again can be potentially employed in adsorbing heavy metal from wastewater. Lu and Su [93] reported that MWCNTs were thermally treated to remove natural organic matter (NOM) in aqueous solution. The amount of adsorbed NOM onto CNTs increased with a rise in initial NOM concentration and solution ionic strength but decreased with a rise in solution pH. Also concluded that the performance of adsorption using raw CNTs and Treated CNTs and granular activated carbon (GAC). Results proved that treated CNTs have the best NOM adsorption performance compared to others.

Besides Zn and Cr, Pb is also one of the famous heavy metals occurring in wastewater. Pb compounds are generally soluble in soft and slightly acidic water. Pb waterworks were often applied in past days and these may still be present in old buildings. The Pb from pipes may partially dissolve in the water flowing through. It occurs in almost all water resources as well as wastewater. Despite its toxicity, the present of lead in the water may affect the human and marine lives' health. Therefore, again, the discussion on the CNTs to absorb lead from wastewater is still going on. Wang *et al.* [94] reported that, the role of functional groups in the adsorption of Pb²⁺ to create a chemical complex was critical for efficient adsorption. 75.3% of Pb²⁺ adsorption capacity was achieved. Pb²⁺ is in the form of PbO, Pb(OH)₂, and PbCO₃ is adsorbed on the surface of the acidified MWCNTs, which is only 3.4% of the total Pb²⁺ adsorption capacity.

They concluded that the Pb²⁺ species adsorbed acidified MWCNTs on the ends and at the defects sites. Wang *et al.* [95] reported that Mn oxide coated carbon nanotubes (MnO₂/CNTs) were used to remove Pb²⁺ from aqueous solution. The Pb²⁺ removal capacity of MnO₂/CNTs decreased with the decrease of pH. From the Langmuir isotherms, maximum adsorption capacity was 78.74 mg/g, comparing with CNTs, significant improvement of Pb²⁺ adsorption shows MnO₂/CNTs can be good Pb²⁺ absorbers. The adsorption of Pb²⁺ by MnO₂/CNTs occurred during the first 15 minutes of contact time, and full equilibrium was reached in 2 hours. The kinetic adsorption described was a pseudo-second-order rate equation.

Wang *et al.* [96], in the study on the adsorption of acidified MWCNTs to Pb^{2+} , found that the experiment met the Langmuir model. Results demonstrated a high adsorption capacity of acidified MWCNTs for Pb^{2+} . The reason stated was the formation of oxygenous functional groups on the surface of the CNTs. Salt formation or complex deposited occurred on the surface of CNTs when acidified MWCNTs react with Pb^{2+} . The adsorption contact time to reach equilibrium is about 20 minutes, which proved to be shorter than AC (reported to be 120 minutes). Besides the discussion on adsorption contact time, authors also stated that Pb^{2+} can be easily regenerated from the acidified MWCNTs by adjusting the solution to pH 2.

In another study, Kabbashi *et al.* [97] discussed the removal of Pb^{2+} , which has reached the maximum value 85% or 83% at pH 5 or 40 mg/L of the CNTs, respectively. Higher correlation coefficients from the Langmuir isotherm model indicates the strong adsorptions of Pb^{2+} on the surface of CNTs (adsorption capacity $X_m = 102$ mg/g). The results indicate that the highest percentage removal of Pb^{2+} (96.03%) can be achieved at pH 5, 40 mg/L of CNTs, contact time 80 minutes and agitation speed 50 rpm.

The effectiveness of an adsorbent depends on the adsorptive properties of its surface. Adsorption takes place when a solid surface is in contact with a solution and tends to accumulate a surface layer of solute molecules created by the imbalanced surface forces. Moradi *et al.* [98] explained the interaction between some heavy metal ions such as Pb^{2+} , Cd^{2+} and Cu^{2+} ions from aqueous solution adsorbed by SWCNTs and carboxylate group functionalized single-walled carbon nanotube (SWCNT-COOH) surfaces.

The maximum adsorption capacities (q_m) for Pb^{2+} , Cu^{2+} and Cd^{2+} ions onto the SWCNT-COOH obtained are 96.02, 77.00 and 55.89 mg/g, respectively, and by the SWCNTs are 33.55, 24.29 and 24.07 mg/g, respectively. The thermodynamic parameters values showed that the adsorption of ions on the SWCNT-COOH and SWCNTs at 283-313 K is spontaneous and endothermic.

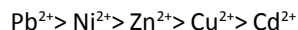
One of the most hazardous heavy metals is cadmium (Cd). In humans, long-term exposure to Cd is associated with severe renal dysfunction. Therefore, it is essential to remove Cd in wastewater treatment. Li *et al.* [99] discussed the adsorption of Cd^{2+} by CNTs. The adsorption capacity is highly pH-

dependent where H_2O_2 oxidizes the CNTs to reach equilibrium state with a high adsorption capacity at lower pH, and it is more obvious compared to the HNO_3 - and $KMnO_4$ -oxidized CNTs. The experiments of the CNT dosage effect on Cd^{2+} adsorption reflect that the adsorption capacity for $KMnO_4$ -oxidized CNTs has a sharper increase at the CNT dosage from 0.03 to 0.08 g per 100 mL than the as-grown, H_2O_2 and HNO_3 -oxidized CNTs and its removal efficiency almost reaches 100% at the CNT dosage of 0.08 g per 100 mL. This shows that CNTs are able to adsorb Cd^{2+} with high adsorption capacity.

To prove the efficiency of CNTs in adsorbing heavy metals, Gao *et al.* [100] studied the adsorption of Ni, Cu, Zn and Cd from aqueous solutions on CNTs oxidized with concentrated nitric acid. The adsorption was carried out in single, binary, ternary and quaternary systems and multicomponent solutions. They studied the effect of process parameters such as the pH value, initial concentration of ions, the surface chemistry of the adsorbent, the kind and number of components in the adsorption system and the ratio of the metal ion species in solution. For the single and binary systems, it turned out that the amount adsorbed on oxidized CNTs followed the order of $Cu^{2+}(aq) > Ni^{2+}(aq) > Cd^{2+}(aq) > Zn^{2+}(aq)$. The good correlation between the amount adsorbed and standard electrode potential indicated that the redox process may serve a role in the mechanism of adsorption. Meanwhile, for the ternary and quaternary systems, the adsorption was more complex. The order of amount adsorbed at the same concentration was $Cu^{2+}(aq) > Cd^{2+}(aq) > Zn^{2+}(aq) > Ni^{2+}(aq)$. Stafiej and Pyrzynska [101] reported that adsorption characteristics of some divalent metal ions (Cu, Co, Cd, Zn, Mn, Pb) was very pH-dependent. The effect of metal ion removal at pH 9 was $Cu^{2+} > Pb^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$.

Li *et al.* [102] studied different heavy metals (Pb^{2+} , Cu^{2+} and Cd^{2+}) adsorption using oxidized CNTs. The maximum adsorption capacities of Pb^{2+} , Cu^{2+} , and Cd^{2+} ions by oxidized CNTs, calculated from Langmuir isotherm, were 63.29, 23.89 and 11.01 mg/g, respectively, in the following order $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The kinetic models of first, pseudo-second- and second-order rate model fit well the experimental data. For initial metal concentration 30 mg/L the adsorption rates of Pb^{2+} , Cu^{2+} and Cd^{2+} are 0.033, 0.049 and 0.096 mg/g.min, respectively, in the order of $Cd^{2+} >$

$\text{Cu}^{2+} > \text{Pb}^{2+}$. Rao *et al.* [103] reported that, the sorption capacities of metal ions to different CNTs follow roughly the order:



The sorption capacities of metal ions by raw CNTs are very low but significantly increased after oxidation of CNT surfaces by HNO_3 , NaOCl , and KMnO_4 solutions. The surface-oxidized CNTs show great potential as superior sorbents for environmental protection applications. The sorption mechanism appears mainly attributable to chemical interaction between the metal ions and the surface functional groups.

The order of heavy metal ions removed from aqueous solutions by CNTs mentioned above shows that their adsorption does not depend clearly on the ionic radius of metal ions, but depend on properties of CNTs such as ionic strength, pH, foreign ions, CNT mass, contact time, initial metal ion concentration, and temperature. However, synthesis conditions have major influences on the nature of the CNTs product formed. Reaction conditions including temperature, gas composition, the nature and composition of metallic catalysts leading to CNTs formation, which, in turn, affect the properties of the final product, still need to be explored in order to understand these influences.

Copper is an essential substance to human life, but in high doses, it can cause anemia, liver and kidney damages as well as stomach and intestinal irritation. This is the reason why copper should not be present in wastewater. Li *et al.* [104] reported that environmental friendly adsorbents that were CNTs immobilized by calcium alginate (CNTs/CA) were designed for copper adsorption. CNTs/CA copper adsorption properties were investigated via equilibrium studies. Experimental results showed that copper removal efficiency of the CNTs/CA is high and reaches 69.9% even at a low pH of 2.1. The CNTs/CA copper adsorption capacity can attain 67.9 mg/g at the copper equilibrium concentration of 5 mg/L.

In other cases, Li *et al.* [105] also studied fluoride adsorption on alumina based CNTs. They reported that the fluoride adsorption isotherms were high at a pH range of 5.0-9.0 with the fluoride adsorption capacity for $\text{Al}_2\text{O}_3/\text{CNTs}$ of about 13.5 times higher than that of the AC-300 carbon and 4 times higher than that of the $\text{c-Al}_2\text{O}_3$ at equilibrium fluoride concentration of 12

mg/L. The broad range of pH values and high adsorption capacity of the $\text{Al}_2\text{O}_3/\text{CNTs}$ indicates its suitability to be applied in fluoride removal from water.

Ruparelia *et al.* [106] reported the removal of heavy metal cations such as cadmium, lead, nickel and zinc by carbon nanomaterials (CNMs), the adsorption capacity of nanocarbon (NC), nanoporous carbon (NPC) and activation were tested. Nanoporous carbon was the best among other adsorbents due to its ion exchange with acidic oxygen containing functional groups introduced by activation during the post-treatment process as well as due to its unique nanoporous structure. They concluded that nanoporous carbon has good potential in water treatment applications. Many CNT applications require handling in solution-phase; however, CNTs have proven difficult to disperse in solvents [107]. Chemical modification of SWCNTs is often required for more versatile suspension capabilities and enablement of certain applications. This has encouraged greater exploitation of their intrinsic properties, as well as the capability to modify these properties. In particular, the functionalization of CNTs is required for their aqueous suspensions and to allow for molecular interactions with biological systems. Native CNTs adsorb surfactants that have been found to associate with CNTs via van der Waals interactions through their hydrophobic chains, rendering CNTs hydrophilic and able to disperse in aqueous environments. SWCNTs can be isolated from aggregated bundles [108], allowing for spectroscopic probing of individual SWCNTs. Surfactant additives prevented nonspecific interactions between SWCNTs and proteins. Also surfactants with modified head groups have also been used to link SWCNTs to specific molecules [109]. Kim *et al.* [110] reported that lipids comprise a class of molecules that interact with CNTs similarly to surfactants. This class of molecule offers control of its interactions with CNTs through modification of their hydrophobic chains, while also providing versatility of the functionality that they impart through the modification of their head groups. Among these lipids, chemical interaction between the heavy metal ions and the surface functional groups of CNTs is the major adsorption mechanism. Tables 1 illustrate the brief summary of the removal of heavy metal ions using non-modified and functionalized CNTs.

Removal of organic dyes

Organic dyes are one of the most hazardous materials in industrial effluents that are discharged from various industries (e.g., textiles, leather, cosmetics, and paper) and act as contaminants to the environment in general and water sources in particular. Many organic dyes have high levels of biotoxicity that cause potential mutagenic and carcinogenic effects in humans. For example, dyes such as Sudan red I, II, III, and VI, whose use in food is prohibited as a result of their toxicity or carcinogenicity at even low concentrations, are widely used in other industries. Most dye compounds contain complex aromatic structures that make them highly resistant to biodegradation and recalcitrant to conventional biological and physical oxidation treatments. Therefore, the targeted removal of such compounds has attracted a growing amount of attention [111].

A wide range of materials has been used for the removal of organic dyes from wastewaters, including AC, zeolite, clay, and polymers, to name but a few. The current priority is to develop novel adsorbent materials with high adsorption capacities and removal efficiencies to realize effective control of these environmental pollutants. CNTs could be one of the most promising adsorbents for this purpose because of their large adsorption capacity for organic dyes. 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 [112].

However, only a few reports on the application of CNTs for dye removal from aqueous solution have been published until now [113-119] and the CNTs were typically directly used without further treatment [114-116, 118] (Table 1). Functionalization of CNTs has been undertaken because the introduction of various functional groups can provide new adsorption sites for organic dyes. Among such modifications, oxidation is an easy method of introducing hydroxyl and carbonyl groups to the sidewalls of CNTs. Oxidized MWCNTs have been shown to be effective in the removal of MR [120] and methylene blue (MB) from aqueous solutions [121]. Another work has focused on the development of CNT-impregnated chitosan hydrogel beads (CSBs) for the removal of Congo red (CR). In Langmuir adsorption modeling, CSBs demonstrated a higher maximum

adsorption capacity than normal chitosan CBs (450.4 vs. 200.0 $\text{mg}\cdot\text{g}^{-1}$; [122]).

A new generation of CSBs prepared by using sodium dodecyl sulfate (SDS) and MWCNTs to improve upon their mechanical properties has also demonstrated a high maximum adsorption capacity for CR (375.94 $\text{mg}\cdot\text{g}^{-1}$ [123]).

Compared to MWCNTs and hybrid CNTs (HCNTs), SWCNTs can demonstrate better adsorption properties for organic contaminants because of their higher specific surface area. Indeed, SWCNTs are more efficient at removing benzene and toluene, and has shown maximum adsorption capacities of 9.98 and 9.96 $\text{mg}\cdot\text{g}^{-1}$, respectively [124]. A maximum adsorption capacity of 496 $\text{mg}\cdot\text{g}^{-1}$ was achieved when reactive blue 29 (RB29) was removed from aqueous solution using SWCNTs [125].

Recently, a novel self-assembled cylindrical graphene-CNT (G-CNT) hybrid was developed, and it achieved a maximum adsorption capacity of 81.97 $\text{mg}\cdot\text{g}^{-1}$ for the removal of MB from aqueous solution, and the removal efficiency reached 97% for low ($10\text{mg}\cdot\text{L}^{-1}$) initial MB concentrations [126]. Lastly, Zeng *et al.* [127] proposed a new concept of using entangled CNTs as porous frameworks to enhance the adsorption of organic dyes. The composites obtained through polymerization with polyaniline (PANI) possessed large surface areas. At an initial malachite green (MG) concentration of $16\text{mg}\cdot\text{L}^{-1}$, the CNT/PANI composites exhibited a 15% higher equilibrium adsorption capacity of 13.95 $\text{mg}\cdot\text{g}^{-1}$ compared to neat PANI. The research on the removal and adsorption of organic dyes using CNTs is summarized in Table 1.

Advantages of CNTs

A critical in-depth analysis has revealed that the morphology, active sites, structural features, curvature of sidewalls, π -conjugative structures are some of the physical properties possessed by CNTs that have enabled them to exhibit enhanced adsorptive properties. Also, their length has been seen to range from nanometers to millimeters with diameters up to 100 nm and having a large specific surface area, high porosity, hollow and layered structures. These unique properties are the cause of strong interactions which allow CNTs to interact with other molecules or atoms through π - π electronic and hydrophobic interactions thereby making them promising adsorbent material [5, 14, 15].

Table 1. Removal of different pollutants using CNTs.

Adsorbent	Removal of pollutants (mg/g) or (%)	Ref.
SWCNTs and MWCNTs ACP	Zn ²⁺ : 43.66; 32.68; 13.04	[62]
As-produced CNTs	Cu ²⁺ : 8.25	[63]
As-produced CNTs	Ni ²⁺ : 18.083	[64]
MWCNTs / iron oxides	Ni ²⁺ : 9.18	[65]
As grown CNTs	Cd ²⁺ : 1.1-3.5	[66]
MWCNTs	Pb ²⁺ : 1	[60]
MWCNTs	Pb ²⁺ : 4	[68]
AC coated with CNTs	Co ²⁺ : 9.0	[69]
CNTs	Cu ²⁺ : 27.03; Cd ²⁺ : 9.30; Pb ²⁺ : 62.50	[70]
CNTs HNO ₃ and NaOCl modified	Cu ²⁺ : 13.87; Cu ²⁺ : 47.39	[63]
Oxidized CNTs	Zn ²⁺ : 58; Cu ²⁺ : 50.37; Cd ²⁺ : 75.84; Pb ²⁺ : 104.05; Co ²⁺ : 69.63	[73]
SWCNTs-COOH	Cu ²⁺ : 65.21; Cd ²⁺ : 50.31; Pb ²⁺ : 78.73	[2]
Oxidized CNTs	Ni ²⁺ : 49.261	[64]
Oxidized SWCNTs and MWCNTs	Ni ²⁺ : 47.85; Ni ²⁺ : 38.46	[76]
Oxidized SWCNTs and MWCNTs	Ni ²⁺ : 47.86; Ni ²⁺ : 38.46	[77]
MWCNTs and SWCNTs	Zn ²⁺ : 14.4; Ni ²⁺ : 13.05	[78]
Oxidized CNTs	Ni ²⁺ : 49.261	[64]
Oxidized CNTs	Cd ²⁺ : 34.36	[79]
Oxidized MWCNTs and e-MWCNT	Cd ²⁺ : 23.32; Cd ²⁺ : 25.7	[80]
Oxidized CNTs	Cd ²⁺ : 11.8	[66]
MWCNTs	Pb ²⁺ : 15.6	[60]
Oxidized MWCNTs	Cu ²⁺ : 28.49; Cd ²⁺ : 10.86; Pb ²⁺ : 97.08	[81]
Oxidized MWCNTs	Pb ²⁺ : 59	[68]
Oxidized MWCNTs	Pb ²⁺ : 91	[82]
Oxidized MWCNTs	Pb ²⁺ : 2.6-11.70	[83]
Oxidized CNTs	Pb ²⁺ : 28	[84]
MWCNTs	Toluidine Blue, Methylene Blue, Methyl Green, and Bromopyrogallol Red	[113]
MWCNTs	Eriochrome Cyanine R: 73.18	[115]
MWCNTs	Alizarin red S: 161.290; Morin: 26.247	[114]
MWCNTs	Reactive red M-2BE: 335.7	[118]
Oxidized MWCNTs	Methyl Orange	[117]
SWCNTs	Reactive Blue 29: 496	[125]

CONCLUSION

Advances in Nanoscale science and engineering are providing new opportunities to develop more cost-effective and environmentally acceptable water treatment technology. CNTs have a number of physicochemical properties that make them particularly attractive for wastewater purification. Recent researches have indicated that CNTs as adsorbents are useful tools for pollutants removal, due to their unique structure and surface characteristics.

In this review, we focused on recent developments related to the removal of metal ions and dyes from aqueous solutions using CNTs.

A survey of the literature on the different methods of surface modification of CNTs reveals a different method have been used to enhance the adsorption performance. To develop environment friendly and inexpensive adsorbents is the key work. With the nanotechnology developed, the exploitation of new efficient adsorption materials is essential and will continue infinitely.

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