Removal of cadmium ion from wastewater by carbon-based nanosorbents: a review

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ABSTRACT

A green environment and a healthy life are dream projects of today's science and technology to save the world. Heavy metal ions in water affect both environment and human health. Cadmium has been identified as one of the heavy metals that causes acute or chronic toxic effects if ingested. Increasing use of cadmium in different technological fields has raised concern about its presence and removal from water/wastewater. Researchers have made many systematic efforts to remove heavy metals from water to reduce their impact on human beings and the environment. Adsorption is one of the best methods to remove heavy metals from water among the different proposed methods. This study explores carbon-based nanosorbents which have been proved as effective adsorbents for removal of cadmium ions from water. The adsorption efficiency of carbon-based nanosorbents is the main criterion to rank and select them for removal of cadmium ions from water. Toxicity, reusability and environmentally friendly characteristics of sorbents are also taken considered while ranking the suitable carbon-based nanosorbents for removal of cadmium ions from water.

Key words | cadmium poisoning, cadmium removal, carbon-based nanosorbents, nanomaterials, purification, water pollution

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INTRODUCTION

Natural waters are mostly polluted by heavy metal ions caused by industrial wastage. Due to their toxic effects metal ions pose a serious threat to living organisms (Khan *et al.* 2008; Singh *et al.* 2010; Zhao *et al.* 2011a, b) and the environment in terms of growth, yield and quality of crops and plants (Singh & Agrawal 2010; Ok *et al.* 2011). Mercury, cadmium, arsenic, chromium and lead have the most serious effects on human beings as well as on the environment. Cadmium is of toxicological concern because of its bioaccumulation and non-biodegradability property even at very low concentration (Waalkes 2000; Li *et al.* 2012; Amin *et al.* 2013). Cadmium is widely used in making nickel-cadmium batteries, pigments, phosphate fertilizers, alloys and metal plating (John & Santhi 1994; Mhiaoui *et al.* 2003; Lambert *et al.* 2007; Martinis *et al.* 2009). Runoff from waste batteries and paints, corrosion of galvanized pipes and discharge from metal refineries are identified sources of cadmium exposure in water (Hutton & Symon 1986; Akesson 2011). Cadmium may be introduced into water naturally by volcanic eruption. The typical permissible cadmium concentration as per the WHO (2008) and EPA (2008) guidelines in drinking water is 0.003 mg/L and 0.005 mg/L, respectively. High concentration of cadmium above the recommended value in water causes serious poisoning in human beings.

Many research groups have focused their interest on removal of heavy metal ions from water/wastewater. A number of methods have been developed to remove heavy metal ions from water, such as ion exchange, reverse osmosis, precipitation, cementation and adsorption (Charerntanyarak 1999; Dabrowski *et al.* 2004; Qdais & Moussa 2004; Hua *et al.* 2012). Among them, adsorption is considered as an effective, efficient and economic method (Sud *et al.* 2008; Lo *et al.* 2012). Among the various traditional adsorbents for water purification, nanosorbents have emerged with great potential and accuracy because of their high surface area

and high efficiency. Nanosized metal oxide, nanocomposites, magnetic nanoparticles and carbon nanotubes have been most effectively used and extensively reviewed for removal of heavy metals from water (Ngomsik *et al.* 2005; Wang *et al.* 2010; Zhao *et al.* 2011a, b; Hua *et al.* 2012; Kumar & Chawla 2014). However, removal of cadmium metal ions by different nanomaterials needs to be studied in greater detail to explore their toxicity, reusability, cost, and maximum efficiency.

This review provides an overview of carbon-based nanosorbents for removal of cadmium from water with the challenge of the environmental impacts, regeneration and reusability characteristics of these nanosorbents. The review is divided into the following sections:

- Cadmium poisoning and health effects
- Nanosorbents for removal of heavy metals from water
- Review of carbon-based nanosorbents for removal of cadmium
- Result analyses
- Conclusions.

CADMIUM POISONING AND HEALTH EFFECTS

Cadmium poisoning is associated with various clinical complications in human beings. Cadmium is a well-known nephrotoxic agent (Wu *et al.* 2008). Cadmium has a very long biological half-time of 10–30 years in humans (Swaddiwudhipong *et al.* 2012) and accumulates primarily in kidney cells with development of chronic disease. The accumulation of cadmium in the kidney leads to dysfunction of the kidney. The ingestion of cadmium in human beings poses a great health risk even at very low concentrations (Waalkes 2003). Kidney damage and lung emphysema are the primary effects of high exposure of cadmium in the body. However, the other target organs that may be affected by the accumulation of cadmium in the body are liver, intestines, placenta, pancreas, heart, skeletal system, immune systems, reproductive system and nervous system (Fowler 2009; Ciarrocca *et al.* 2013). Cadmium poisoning sometimes causes hypertension, diabetes, nerve or brain damage, liver disease and urinary stones (Horiguchi *et al.* 2004; Fowler 2009). Cadmium poisoning may also cause bone damage

(Jarup & Akesson 2009) and affects teeth and the nervous system permanently by replacing calcium. Long-term exposure to cadmium and excessive intake of cadmium causes serious illnesses such as itai-itai disease in human beings (Bolan *et al.* 2013). In addition, recently cadmium has been identified as a human carcinogen; increasing concentrations of cadmium in water increases cancer risk in humans (Mahalik *et al.* 1995; Fowler 2009).

NANOSORBENTS FOR REMOVAL OF HEAVY METALS FROM WATER

Toxic heavy metal ions removal from water/wastewater by using synthetic compounds, polymers and other materials as sorbents is of great concern in environmental research applications (Moradi *et al.* 2009; Fu & Wang 2011). A number of traditional sorbents have been used for removal of cadmium from water/wastewater. Agricultural waste materials such as stems (Tan & Xiao 2009), husks (Panda *et al.* 2006), bark (Ghodbane *et al.* 2007), shell (Cimino *et al.* 2000), peels (Li *et al.* 2007), leaves (Sharma & Bhattacharyya 2005) and saw dust (Memon *et al.* 2007) have been extensively used as traditional sorbents for removal of cadmium. However, the use of traditional sorbents has been restricted by the inconvenience of separation in multimetal ions solution, poor performance and efficiency. Over the last decade nanomaterials have been extensively studied for their potential applications in various applied fields, such as energy application, quantum dots for biomedical application, and photocatalytic applications (Krishna *et al.* 2013; Han & Ho 2014; Lee & Jang 2014). The sorption potential of nanomaterials has not been studied extensively. Nanomaterials are a promising material in terms of separation, performance and efficiency for removal of heavy metals from water because of their unique properties, such as small size, high specific surface area and morphological features (Hua *et al.* 2012). Nanomaterials have been found to be superior sorbents for various organic and inorganic pollutants, such as benzene (Gauden *et al.* 2006), fluoride and ethidium bromide (Li *et al.* 2003c; Najafi *et al.* 2013). The synthetic method of nanomaterials has been intensively developed and designed not only for their fundamental scientific interest but also their important application in

sorption fields in order to get maximum efficiency (Shamsudin *et al.* 2013). The sorption capacity of nanomaterials was found to be improved by oxidation, modification or functionalization on the surface of nanomaterials (Khani & Moradi 2013). The European Commission on 18 October 2011 adopted the definition of a nanomaterial as a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions are in the size range 1–100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%. A number of carbon-based nanoparticles, nanometal oxides, magnetic nanoparticles, nanocomposites, dendrimers, zeolites, nanoclays and modifications of functionalized nanomaterials have been widely used as adsorbent to remove heavy metal ions from water or wastewater (Hu *et al.* 2006; Ghorbani & Eisazadeh 2013).

REVIEW OF CARBON-BASED NANOSORBENTS FOR REMOVAL OF CADMIUM

Carbon-based nanomaterials include carbon nanotubes, oxidized carbon nanotubes, carbon-based fibres, graphene, carbon nanocomposites and fullerene. Raw carbon-based nanomaterials and modified carbon-based nanomaterials have been extensively used for removal of heavy metal ions from water. The following section describes the detailed study of carbon-based nanomaterials used as nanosorbent for removal of cadmium ions from water/wastewater.

Carbon nanotubes

The study of adsorption properties of carbon nanotubes (CNTs) plays an important role in the advance of research and technology for water purification. The applications of CNTs for the removal of heavy metal ions from aqueous systems have been extensively studied because of their large specific surface area (3,000 m^2/g), mechanical stability and highly porous structure (Yin *et al.* 1999; Sheikh 2008; Moradi *et al.* 2012). Heavy metal ion adsorption capacity of

CNTs is directly related to their total active surface acidity. Generally, CNTs can be synthesized by electric arc discharge, pulse laser vapour and catalytic decomposition of gaseous hydrocarbons (Ando *et al.* 2004; Balasubramanian & Burghard 2005). CNTs synthesized by two-stage catalytic chemical vapour deposition (CVD) method gives the highest aspect ratio, renders the lowest integrated intensity ratio and diameter size distribution, and provides excellent purity of CNTs (Shamsudin *et al.* 2013). Defects on the walls of CNTs decrease their adsorbent capacity. The sorption capacity of Cd^{2+} ion onto 10 mg of CNTs dosage of the average diameters in the range of 20–30 nm and 0.789 mg/L initial concentration observed was 19.14% at pH 7.0 for 120 minutes of contact time (Kabbashi *et al.* 2011). On the other hand, CNTs were grown on the surface of micro-sized Al$_2$O$_3$ particles for removal of Cd^{2+} and other heavy metal ions from aqueous solutions (Hsieh & Horng 2007). The adsorption capacity of CNTs grown on Al$_2$O$_3$ was superior to that of active carbon powders, commercial carbon nanotubes and Al$_2$O$_3$ particles. Although the absorption capacity of Cd^{2+} ion on CNTs grown on Al$_2$O$_3$ was lower than the Pb^{2+} and Cu^{2+} ions, it could be increased by further treatment or oxidation. The calculated saturation amount for Cd^{2+} was 2.0, 6.19 and 8.89 mg/g, adsorbed by 1 g of Al$_2$O$_3$, commercial CNTs and CNTs grown on Al$_2$O$_3$ respectively.

Different oxidizing reagents such as HNO$_3$, H$_2$O$_2$ and KMnO$_4$ were used for oxidation of CNTs (Khani & Moradi 2013). Oxidized CNTs show exceptionally high adsorption capacity and efficiency for removal of heavy metal ions. Enhancement in the adsorption capacity and efficiency of oxidized CNTs is explained due to incorporation of the oxygen containing functional groups on the surface of CNTs by chemical oxidation. Carboxylic and phenolic groups present on the carbon surface exhibit high affinity for various metal ions in water (Kadirvelu & Namasivayam 2003). Langmuir maximum adsorption capacity of Cd^{2+} ion onto oxidized carbon nanotube was higher than other metal ions such as Co^{2+}, Zn^{2+}, and Cu^{2+} (Gao *et al.* 2009; Tofighy & Mohammadi 2011). The adsorption efficiency of oxidized CNTs for cadmium and other metal ions has also been investigated in single, binary, ternary and quaternary systems (Gao *et al.* 2009). The amount of Cd^{2+} ions adsorbed on the oxidized CNTs was higher than

the Zn^{2+} for single and binary systems. However, the adsorption process became more and more complicated for ternary and quaternary systems and showed a different order. Ion exchange or outer-sphere surface mechanism was suggested to be predominant over the complex mechanism of the removal process. However, ion exchange or outer surface mechanism mainly contributes to Cd^{2+} uptake on oxidized multi-walled carbon nanotubes (MWCNTs) at low pH and inner-sphere surface mechanism is the main uptake mechanism at high pH values (Yang *et al.* 2012). The effect of different oxidizing reagent on carbon nanotubes was also investigated to find out the maximum adsorption capacity of Cd^{2+} ion from aqueous solution. Three oxidizing reagents, H_2O_2, $KMnO_4$ and HNO_3, have been used to compare the adsorption efficiency of oxidized CNTs (Li *et al.* 2003b). As compared to CNTs, $KMnO_4$ oxidized CNTs showed high absorption capacity. The adsorption capacity of Cd^{2+} on CNTs was only 1.1 mg/g at a 4 mg/L Cd^{2+} ion equilibrium concentration while it reached 2.6, 5.1 and 11.0 mg/g for the H_2O_2, HNO_3 and $KMnO_4$ oxidized CNTs, respectively, at the same concentration. Adsorption capacities for three types of oxidized CNTs were greater because oxidation of CNTs introduces functional groups on the surface and increases the surface area. The specific surface area of H_2O_2, $KMnO_4$ and HNO_3 oxidized carbon nanotubes was found to increase from 122 to 130, 128 and 154 m^2/g, respectively, by the oxidation process. The adsorption capacity of Cd^{2+} for $KMnO_4$ oxidized CNTs was sharply increased with increasing the dosage of CNT because host manganese residuals on oxidized CNTs surface by $KMnO_4$ contribute to cadmium sorption. Furthermore, the adsorption capacities and efficiency of cadmium ion also depend on the type of CNTs, i.e., single-walled carbon nanotubes (SWCNTs) and MWCNTs.

Single-walled carbon nanotubes are composed of a single rolled-up graphene sheet and MWCNTs are composed of a concentric arrangement of many cylinders. In a graphite arc process that forms fullerenes from atomized carbon, multi-walled CNTs are deposited at the graphite anode (Iijima 1991). Single-walled carbon nanotubes were also synthesized in the presence of metal catalyst (Iijima & Ichihashi 1993). Limited work has been done on the removal of cadmium ion by SWCNTs and modified SWCNTs. The removal efficiency of Cd^{2+} ions by SWCNTs has been investigated in detail only by Moradi (Moradi *et al.* 2010, 2011; Moradi 2011; Moradi & Zare 2011). Langmuir maximum adsorption capacity of Cd^{2+} ion observed was 24.07 mg/g on SWCNT at pH 5.0–6.0. The degree of sorption with respect to temperature on the sorbent surface has been explained on the basis of thermodynamic parameters, such as change in free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS). The negative value of free energy of adsorption indicates the feasibility of the process. However, a negative value of enthalpy of adsorption shows an exothermic process and a positive value of enthalpy of adsorption shows an endothermic process. The positive value of entropy of adsorption indicated spontaneous sorption process with high affinity (Tadjarodi *et al.* 2013). Thermodynamic parameters values showed that the adsorption process of ions was taking place by physi-sorption on the surface of SWCNTs and was spontaneous and endothermic in nature at 283–313 $°K$ (Moradi *et al.* 2010, 2011).

Multi-walled carbon nanotubes are formed by two or more rolled-up graphite sheets. The available adsorption space is either external surface or inter-wall spaces, i.e., the spaces between the coaxial tubes of MWCNTs (Yang & Xing 2007). Three carbon-based materials including MWCNTs (5–10 nm), activated carbon (AC) and carbon encapsulated magnetic nanoparticles (CEMNPs) (40–90 nm) were used for the comparative study of cadmium adsorption under similar conditions (Pyrzynska 2010). The results showed that the theoretical saturation capacity for cadmium was 9.91, 20.37 and 91.0 mg/g for AC, CNTs and CEMNPs, respectively, at pH 8.0. High adsorption capacity of CEMNPs towards cadmium ions was explained by the synergistic effect between CNTs and iron oxides which improves the affinity of the adsorbent. The results indicate that specific active sites on the sorbents play an important role in metal ions' retention. There was competition among the different heavy metal ions for binding of the active sites present on the MWCNTs' surface. However, it was found that Cd^{2+} ion has slightly low affinity for binding of the active sites present on the MWCNTs' surface compared to other metal ions such as Cu^{2+}, Zn^{2+} and Pb^{2+} (Li *et al.* 2003a; Salam *et al.* 2012). The spontaneity of the adsorption process was confirmed by the calculated

thermodynamics parameters (Salam 2013). Calculated thermodynamics parameters showed that the value of the free energy was negative while the change in entropy value was positive for cadmium ions. Positive value of entropy is due to the physical adsorption of cadmium ions from the aqueous solution to the surface of carbon nanotubes which increases randomness on the surface.

Modified carbon nanotubes

Modification on the surface plays an important role in increasing the sorption capacity of CNTs. It was found that amines with oxygen containing groups on the surface might be coordinating sites for sorption of heavy metal ions (Vukovic *et al.* 2011; Wang *et al.* 2013). The surface modification of CNTs can be done either by chemical bond formation or by physical adsorption (Wildgoose *et al.* 2006). Nanotubes are slightly less stable in polar solvents and tend to aggregate in solution. Surface modification also helps in stabilizing the dispersion in solvents and imparts high stability in solution. Both SWCNTs and MWCNTs were modified with different groups to increase the sorption capacity of CNTs for removal of heavy metals. The adsorption properties of carbon nanotubes were significantly improved by modification with different groups for removal of cadmium metal ions. Different parameters such as effects of temperature, pH, ionic strength, metal ion concentration and the amount of modified CNTs were studied for adsorption of heavy metal ions from water. The interaction of cadmium metal ions with carboxylate group functionalized single-walled carbon nanotube (SWCNT-COOH) surface was found to be higher than the single-walled carbon nanotube (SWCNT) surface due to the carboxyl group which increases negative charge on carbon nanotube surface (Moradi *et al.* 2011). Also, surface functionalization improved their stability in water and adsorption efficiency towards heavy metal ions (Li *et al.* 2003a; Feng *et al.* 2008). Langmuir maximum adsorption capacity of Cd^{2+} ion was increased from 24.07 to 55.89 mg/g on SWCNT-COOH at pH 5.0–6.0. Thermodynamic parameter values showed that adsorption processes of ions was taking place by chemi-sorption on the surface of SWCNTs-COOH and physi-sorption on the surface of SWCNTs and were spontaneous and endothermic

in nature at 283–313 °K (Moradi *et al.* 2010, 2011; Moradi 2011; Moradi & Zare 2011).

The adsorption properties of MWCNTs were significantly improved by modified multi-walled carbon nanotubes with different groups such as six-arm amino polyethylene glycol (PEG), 8-hydroxyquinoline, ethylenediamine (En) (Vukovic *et al.* 2010; Kosa *et al.* 2012; Salam 2013; Velickovic *et al.* 2013). The maximum adsorption capacities of Cd^{2+} ions on the surface of modified MWCNTs by six-arm amino PEG (MWCNTs-PEG) was 77.6 mg/g for initial cadmium ion concentration of 10 mg/L at pH 8.0 (Velickovic *et al.* 2013). Minimum adsorption was observed at lower pH because at lower pH high concentration of hydrogen ions are present and, according to surface complex formation theory, hydrogen ions are preferentially adsorbed rather than the metal ions (Kosa *et al.* 2012). The percentage adsorption of Cd^{2+} ions increased from 14.3 to 61.7% by MWCNTs and from 40.67 to 100% by modified multi-walled carbon nanotubes when pH increases from 6.0 to 9.0 because cadmium usually precipitates at higher pH values (Lv *et al.* 2005). Intra-particular Weber–Morris kinetic model was used to describe the time-dependent adsorption. The initial adsorption reached equilibrium gradually at 97% of cadmium adsorption by physic-sorption process.

The MWCNTs with very few oxygen containing functional groups showed relatively low sorption capacities for Cd^{2+} (Tian *et al.* 2012). The sorption capacity of Cd^{2+} ions by MWCNTs was increased by surface coating with manganese dioxide (MnO_2), (MWCNTs-MnO_2) or with humic acids (Yang *et al.* 2011; Tian *et al.* 2012; Luo *et al.* 2013). Surface coating with four sequentially extracted humic acids on three multi-walled CNTs (MWCNTs) with different surface areas affected the adsorption process of heavy metal ions significantly. However, surface coating with the humic acids lowered the surface areas of the MWCNTs but greatly increased their sorption capacities because of complexation and electrostatic attraction (Tian *et al.* 2012). Surface coating with the humic acids introduced oxygen containing functional groups and increased negative charge on the MWCNTs' surface. The adsorption efficiency of multi-walled carbon nanotubes for the removal of heavy metal ions could also be increased by modification with chitosan (Salam *et al.* 2011). Two real water samples were collected

from the Red Sea and a wastewater treatment plant to evaluate the applicability of the nanosorbent (Kosa *et al.* 2012). Most of the metal ions were removed from the solution by using modified MWCNTs with 8-hydroxyquinoline. When MWCNTs were used to remove metal ions, only 0.3% Cd^{2+} ions were removed while modified MWCNTs had a high affinity for the removal of Cd^{2+} ions (5.77%) from real water samples (Kosa *et al.* 2012). If we look at the mechanism of ion removal, cadmium ions are removed from the water by ion-exchange as well as adsorption mechanisms. In the ion-exchange mechanism, cadmium ions are exchanged with the protons present on the oxygen atoms of the sidewall functional groups of carbon nanotubes (Figure 1). However, adsorption of cadmium ions on the surface of CNTs is due to strong chemical interaction between the cadmium ions and the surface sites of carbon nanotubes and is known as inner-sphere adsorption, while weaker interaction between cadmium ions and the surface sites of CNTs is known as outer-sphere adsorption.

Graphene

Graphene possesses a two-dimensional structure of one- or multi-atomic-layered graphites. Graphene is used as another carbon-based nanosorbent, which has good thermal and mechanical properties. A few-layered graphene oxide nanosheets (GOx) were prepared by modified Hummers method which introduces –COOH, $-C=O$ and –OH groups on the surface to increase the sorption capacity of heavy metal ions. Cadmium sorption on graphene oxide nanosheets was carried out in the presence of $NaClO_4$ in polyethylene test tubes (Zhao *et al.* 2011b). The sorption of Cd^{2+} increased with increasing pH from 6 to 9 because of deprotonation at high pH which made the surface more negative to combine with metal ions. The maximum sorption capacity of Cd^{2+} was 106.3 mg/g at pH 6.0 (303 °K). However, the sorption of Cd^{2+} on graphene oxide nanosheets decreased with increasing pH in the presence of humic acid because of formation of soluble metal–humic acid complex.

Modified or functionalized graphene was also used for removal of Cd^{2+} ions from water samples. Magnetic graphene oxide nanocomposite was synthesized for simultaneous removal of Cd^{2+} ions and ionic dyes such as methylene blue and orange G (Deng *et al.* 2013). The maximum sorption capacities in ultrapure water for Cd^{2+} ion was 91.29 mg/g. The sorption capacity of nanocomposite was suppressed for Cd^{2+} in the presence of methylene blue dye. The sorption capacity for Cd^{2+} ion in tap water samples was 65.39% of that in ultrapure water. Functionalized graphene was also fabricated by electrolysis method with potassium hexa-fluorophosphate solution as electrolyte under the static potential of 15 V (Deng *et al.* 2010). Langmuir maximum adsorption capacity observed was
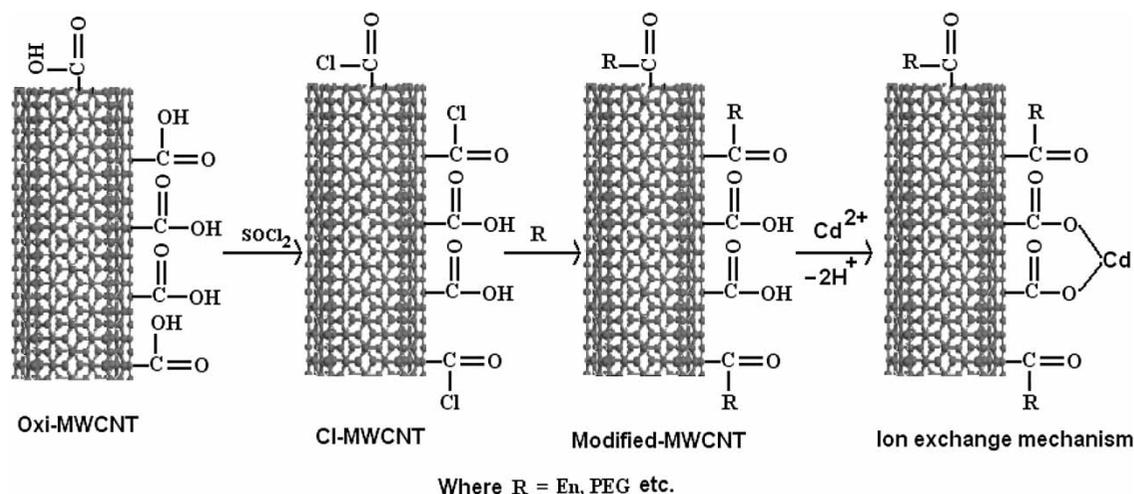
Figure 1 │ Schematic diagram of functionalization of carbon nanotubes sidewall and ion exchange with sidewall groups by cadmium ions in solution.

73.42 mg/g at pH 6.2 and the adsorption equilibrium was achieved in just 40 minutes for cadmium ions. Iron-iron oxide dispersed graphene was used for removal of Cd^{2+} ions from water samples (Bhunia *et al.* 2012). Iron oxide nanoparticles in the presence of H_2/Ar atmosphere were transformed to a matrix of iron-iron oxide on the graphene surface at an elevated temperature. Iron-iron oxide dispersed graphene was highly porous and robust. Iron-iron oxide matrix dispersed on reduced graphene oxide (rGO), $rGO–Fe(0)–Fe_3O_4$, with high surface area and high efficiency was basically used for removal of arsenic metal from water samples but it was also used to evaluate adsorption efficiency of other toxic heavy metals like Cd^{2+} and Hg^{2+} from water. The maximum adsorption capacity of this sorbent was slightly poor towards Cd^{2+} ions because the standard reduction potential of Cd^{2+} (-0.35 V) was more negative than the other metal ions.

Carbon-based nanocomposites

It is possible to assemble the nanoscale units in nanocomposites in order to explore their properties. In carbon nanocomposites active materials can be dispersed into a carbon matrix or nanocarbon can be dispersed into a polymer. Various magnetic nanocomposites with carbon-coated nickel structure have been used for removal of heavy metals from water (Xiao *et al.* 2012). Sankararamakrishnan *et al.* (2014) synthesized nanofloral clusters (NFCs) of CNTs over iron and nickel doped activated alumina by CVD for removal of cadmium ion from water. Langmuir maximum adsorption of Cd^{2+} ion on nanofloral clusters of CNT (NFC-CNT) was 229.9 mg/g at pH 7.5. A solid-phase extraction method for separation and pre-concentration determination of Cd^{2+} ion in environmental samples has been developed by using multi-walled carbon nanotubes/poly(2-amino-thiophenol) nanocomposites (MWCNT-NC) (Nabid *et al.* 2012). The sorbent showed high adsorption affinity for heavy metal ions on macromolecular chains due to the presence of numerous good extractive sites (S and N) of conducting polymer. The maximum adsorption capacity of sorbents at optimum conditions for cadmium ions was found to be 178.7 mg/g at pH 6.0 with the detection limit of 0.3 ng/mL. Recently, nanocarbon conjugated polymer nanocomposites (NCPCs) were prepared for effective removal of heavy metal ions from water (Khaydarov *et al.* 2010). NCPNs were synthesized from nanocarbon colloids and polyethylenimine. The bonding capacity of NCPC was 5.7 mmol/g at pH 6.0 for most of the divalent metal ions. The sorption percentage of Cd^{2+} and other divalent metal ions was higher than 99%. A novel composite of silver with multi-walled carbon nanotubes (Ag-MWCNTs) has been synthesized from functionalized multi-walled carbon nanotubes reduced with N,N-dimethylformamide and cross-linked with silver nitrate for effective removal of Cd^{2+} ion (Ramana *et al.* 2013). The Langmuir isotherm model was consistent with the experimental data at different temperatures. Maximum adsorption of Cd^{2+} ion was observed at pH 7.0 (more than 90% removal, 10 mg/L initial concentration of cadmium). The thermodynamic parameters indicated that the adsorption process of Cd^{2+} ion onto Ag-MWCNTs was endothermic, spontaneous and feasible in the temperature range 293–313 °K.

RESULT ANALYSES

The reported concentration of cadmium in different environmental water samples is more than the recommended permissible concentration as per WHO guidelines (0.003 mg/L). The reported concentration of cadmium in different environmental water samples are in the range of 0.002–1.46 mg/L (Igwilo *et al.* 2006; Akoteyon 2012; Ambedkar & Muniyan 2012). High concentration of cadmium in water causes different poisonous effects on human beings. Therefore, traditional and nanomaterials are used for removal of cadmium ions from water. Carbon-based nanosorbents are preferred over conventional carbonaceous sorbents because of their high surface area to volume ratio, controlled pore size distribution and they are easy to fabricate on the surface to enhance surface chemistry. Adsorption on the surface of carbon-based nanosorbents is driven by hydrophobic dispersion and weak dipolar forces. This section describes the ranking of carbon-based nanosorbents for removal of cadmium ions on the basis of different parameters and detailed study of adsorption isotherms and kinetics of adsorption of the cadmium ions on carbon-based nanosorbents.

Ranking of carbon-based nanosorbents for removal of cadmium

The removal efficiency of different synthetic, naturally occurring and waste materials used as adsorbents was 10–80% with respect to the initial cadmium ion concentration. However, adsorption capacity of these materials can be significantly increased by chemical modification on the surface or by pretreatment methods (Rao *et al.* 2010). Various adsorption parameters are required to evaluate their effects on removal efficiency and ranking of carbon-based nanosorbents for removal of cadmium ions from water samples. The adsorption capacity of different carbon-based nanosorbents has been compared at pH 5.0–7.5 and temperature range of 25–30 °C for their selection for treating real water samples. Available important data up to the present is listed in Table 1. Solution pH plays a key role for removal of cadmium from water and wastewater. As can be seen from the reviewed analysis, the removal efficiency of Cd^{2+} for all reviewed carbon-based materials tended to increase with increasing pH value. Increasing pH value could precipitate metal as metal hydroxide and the functional groups on the sorbent surface exist in the deprotonated form. However, at low pH, higher concentration and mobility of hydrogen ions favoured hydrogen ions' adsorption rather than metal ions on adsorbent surfaces. The percentage adsorption of Cd^{2+} ions increased up to 100% by modified multi-walled carbon nanotubes with 8-hydroxyquinoline when pH increases from 6.0 to 9.0. However, the adsorption capacity of carbon-encapsulated magnetic nanoparticles (CEMNPs) was also better as compared to other reviewed carbon-based nanosorbents at higher pH value. Also, the removal efficiency of Cd^{2+} increased up to a limit range with increasing the temperature and time, respectively.

The adsorption capacity of the reviewed carbon-based nanosorbents at pH 5.0–7.5 follows roughly the following order: modified or dispersed MWCNTs > graphene oxide > SWCNTs-COOH > SWCNTs > oxidized CNT > MWCNTs > CNTs (Figure 2). However, the adsorption capacity of carbon-based nanosorbents precisely depends on the type of nanosorbents, e.g., non-functionalized and functionalized nanosorbents. The adsorption capacity of non-functionalized carbon nanotubes (CNTs) follows the following

order: oxidized-CNT > CNTs-Al$_2$O$_3$ > CNTs. Oxidized raw CNTs gave better results in comparison to raw CNTs because of more active oxygen containing groups on the surface of CNTs. The adsorption capacity of functionalized or dispersed multi-walled CNTs follows the following order: NFC-CNT > MWCNTs-NC > MWCNTs-PEG > MWCNTs-MnO$_2$ > MWCNTs-En > MWCNTs. Modification or dispersion of CNTs can considerably increase the surface area as well as more active sites on the surface. The results analysis also showed that SWCNT-COOH surfaces were more effective toward Cd^{2+} ion adsorption than SWCNTs surface because of the carboxyl group which increases negative charge on carbon nanotubes surface. However, SWCNTs offered better performance regarding Cd^{2+} ion adsorption than the MWCNTs because of the presence of more active sites on the surface of SWCNTs. It is very difficult to correlate all the reviewed results in terms of all parameters because of their different preparation conditions, purification methods, various size and surface areas of reported sorbents.

The choice of nanosorbents for removal of cadmium also depends on toxicity and reusability of the carbon-based nanosorbents. Although a number of *in vitro* and *in vivo* toxicological studies have been performed, toxicity of carbon nanotubes has not been significantly evaluated because of the number of factors involved. Toxicity of carbon nanotubes depends on many factors, such as their physical form, diameter, length and the nature of attached molecules on the sidewall or surfaces (Wang *et al.* 2009; Firme & Bandaru 2010; Kolosnjaj *et al.* 2010). Also, the results of toxicity are often conflicted at the cellular and whole body levels. The size and length control of CNTs is very important to control the toxicity. Chronic toxicity of CNTs can be reduced by using short CNTs and keeping their length to less than 5 μm (Chawla & Kumar 2013). The functionalization on the surface of carbon nanotubes improves their biocompatibility and reduces the toxic effects (Chawla & Kumar 2014). It was found that at a particular concentration, surface modification or functionalization reduce the toxicity of carbon nanotubes (Foldvari & Bagonluri 2008). Thus, it can be concluded that modified or functionalized carbon nanotubes with smaller size and smaller length may be the best sorbent for removal of cadmium metal ions in terms of toxicity. In addition, further studies are required in this area to make these materials safer and

Table 1 | Carbon-based nanosorbents for removal of cadmium metal ions from aqueous solution

Carbon-based adsorbent	Preparation method	Max. ads. capacity of Cd^{2+} (mg/g)	Other target metal ions M(II)	Temp. (K)	pH	Surface area (m^2/g)/Particle size (nm)	Reg. coeff. (R^2)	Isotherms/ Kinetics	Reference
Carbon nanotubes (CNTs)	Commercially available	1.1	–	298	5.5	122/–	–	–	Li *et al.* (2003b)
(CEMNPs)	Carbon arc plasma	91.0	–	Room temp. (RT)	8.0	–/40–90	0.998	Langmuir/ Pseudo-second-order	Pyrzynska (2010)
CNTs on micro-sized Al_2O_3	Electroless plating in CH_4 atmosphere at 700 °C	8.89	Pb, Cu	RT	6.6	18.61/30–80	0.956	Langmuir/ Pseudo-second-order	Hsieh & Horng (2007)
$KMnO_4$ oxidized CNTs	Oxidation method	11.0	–	298	5.5	128/10–30	–	–	Li *et al.* (2003b)
SWCNT	Chemical vapour deposition	24.07	Pb, Cu	293	5.0	400/1–2	0.999	Langmuir/–	Moradi *et al.* (2011)
SWCNT-COOH	Purchased from NanoAmor Nanostructured & Amorphous Materials, Inc., USA	55.89	Pb, Cu	293	5.0	400/1–2	0.999	Langmuir/–	Moradi *et al.* (2011)
MWCNTs	Commercially available	10.86	Pb, Cu	RT	5.0	–	0.998	–	Li *et al.* (2003a)
MWCNT-PEG	MWCNTs + oxidation by $SOCl_2$ + amination by $PEG-NH_2$	77.60	Pb, As(V)	298	4.0	22.4/17.4	0.999	Koble–Corrigan/ Weber–Morris	Velickovic *et al.* (2013)
MWCNT-En	Chemical modification	25.7	–	298	8.0	–	0.999	Langmuir/ Pseudo-second-order	Vukovic *et al.* (2010)
MWCNT-NC	Chemical method	178.70	Pb	RT	6.0	–	–	–	Nabid *et al.* (2012)
MWCNT-MnO_2	Chemical method	41.6	–	298	6.0	–	0.999	Langmuir/ Pseudo-second-order	Luo *et al.* (2013)
Layered Gox	Hummers method	106.3	Co	303	6.0	–	0.999	Langmuir/–	Zhao *et al.* (2011a)
NFC-CNT	Chemical vapour deposition	229.9	Cr(VI)	–	7.5	–	0.999	Langmuir/–	Sankararamakrishnan *et al.* (2014)
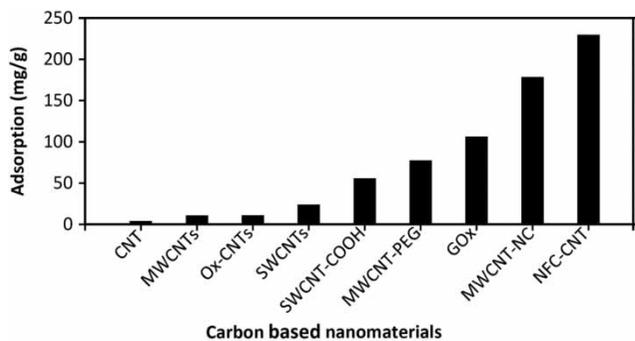
Figure 2 │ Adsorption of cadmium by different carbon-based nanomaterials from water samples at pH 4.0–7.5 and temperature range 25–30 °C.

compatible for different applications. Regeneration is another very important aspect for ranking of these nanomaterials. Carbon nanotubes can be regenerated and reused for removal of heavy metal ions. Regeneration significantly reduces the overall costs of the procedure. Regeneration and recycling of carbon nanotubes were evaluated in detail for a number of heavy metal ions (Wang *et al.* 2007; Tehrani *et al.* 2013). There are very few studies available to date for regeneration of carbon nanotubes for cadmium metal ions (Hsieh & Horng 2007; Kosa *et al.* 2012). Most of the metal ions desorbed on the surface of carbon nanotubes in acidic medium (pH lower than 2.0) and could be used without losing efficiency for up to three cycles. Research adopting standard and similar procedures while considering all parameters in all aspects is further required for finding the most efficient, cheapest and safest alternatives for removal of cadmium ions from water.

Adsorption isotherms of carbon-based nanosorbents

Langmuir and Freundlich adsorption isotherms are quite helpful in determining the adsorption capacity of an adsorbent (Li *et al.* 2004; Hsieh & Horng 2007). In the reviewed nanosorbents, the Langmuir isotherm gave the better value of regression coefficient ($R^2 \sim 0.999$) compared to Freundlich isotherm ($R^2 \sim 0.979$) which indicates monolayer coverage of the cadmium ions on the surface of the adsorbent (Lv *et al.* 2005; Moradi *et al.* 2010; Pyrzynska 2010; Kabbashi *et al.* 2011; Moradi & Zare 2011; Zhao *et al.* 2011a, b). It is based on the assumption that maximum adsorption occurs when a saturated monolayer of metal ions is present on the adsorbent surface. The Langmuir equation

(Langmuir 1918) for monolayer coverage of the metal ions on the surface of the adsorbent is expressed as follows:

$$q_e = (q_m K_L C_e)/(1 + K_L C_e) \tag{1}$$

A linear form of the Langmuir equation can be expressed as:

$$C_e/q_e = 1/(q_m K_L) + C_e/q_m \tag{2}$$

where q_e is the equilibrium amount adsorbed (mg/g), q_m is maximum adsorbed metal ion amount to complete monolayer coverage (mg/g), K_L is Langmuir constant related to energy of adsorption, C_e is equilibrium concentration of metal ions (mg/L). The value of K_L is used to calculate essential characteristics of Langmuir isotherms called dimensionless separation parameter R_L (Hall *et al.* 1966; Annadurai & Krishnan 1997):

$$R_L = 1/(1 + K_L C_0) \tag{3}$$

where K_L is Langmuir constant and C_0 is initial concentration of metal ions in (mg/L). The value of separation factor indicates shape or type of isotherms. Isotherm will be linear if $R_L = 1$, irreversible if $R_L = 0$, favourable if $0 < R_L < 1$ and unfavourable if $R_L > 1$. The value of separation factor and regression coefficient calculated by the Langmuir isotherms model for most of the carbon-based nanomaterials is less than 1 ($R_L < 1$ and $R^2 \sim 0.999$) which indicates favourable and mono-layered coverage of the cadmium ions on the surface of the carbon-based nanosorbents (Li *et al.* 2004; Lv *et al.* 2005; Hsieh & Horng 2007; Moradi *et al.* 2010; Pyrzynska 2010; Vukovic *et al.* 2010; Kabbashi *et al.* 2011; Moradi & Zare 2011; Luo *et al.* 2013).

The Freundlich isotherm is basically an empirical relationship used to describe the adsorption on heterogeneous adsorbent surface (Freundlich 1906). The Freundlich equation can be expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where q_e is the equilibrium amount adsorbed (mg/g), K_F and n are Freundlich constants corresponding to adsorption

capacity and adsorption intensity respectively. A linear form of the Freundlich equation can be expressed as:

$$\log q_e = \log K_F + 1/n \log C_e. \tag{5}$$

The value of n varies in the range of 1–10 for classification of favourable adsorption (Chantawong *et al.* 2003). The high value of $1/n$ indicates preferential and high adsorption intensity toward adsorbent (Li *et al.* 2004). However, the high value of Freundlich constants K_F indicates greater adsorption tendency toward adsorbent. In some cases the adsorption process of cadmium ions on adsorbent surfaces has been described by the Koble–Corrigan adsorption isotherm which is a three-parameter equation incorporating Langmuir and Freundlich adsorption isotherms (Velickovic *et al.* 2013). The Koble–Corrigan adsorption isotherm is also used for heterogeneous adsorbent surface (Koble & Corrigan 1952). The values of regression coefficients (R^2) calculated by the Langmuir model were higher for most of the carbon-based nanosorbents compared to the Freundlich model. Therefore, adsorption of cadmium ions on most of the carbon-based nanosorbents is defined by Langmuir isotherms implying the monolayer coverage of the cadmium ions on the surface of the carbon-based nanosorbents.

Kinetic study of carbon-based nanosorbents

Adsorption of metal ions on the adsorbent surfaces can be easily explained by different kinetic models, e.g., pseudo-first-order (Lagergren 1898), pseudo-second-order (Demirbas *et al.* 2002) and diffusion or intra-particle diffusion kinetic models (Weber & Morris 1963). Kinetic models are also helpful to describe the mechanism of adsorption of metal ions on the adsorbent surface. The pseudo-first-order kinetic model was given by Lagergren in 1898 for solid–liquid system and can be expressed by:

$$dq_t/dt = k_1(q_e - q_t) \tag{6}$$

A linear form of the equation is:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{7}$$

where k_1 is the adsorption rate constant of first-order kinetic models in L/mg/min, q_e is equilibrium amount adsorbed at time t (mg/g) and q_t is equilibrium amount adsorbed at time $t = \infty$. The values of k_1 were calculated from the slope of the linear plot of $\ln(q_e - q_t)$ versus t.

The pseudo-second-order kinetic models can be expressed by (Demirbas *et al.* 2004):

$$dq_t/dt = k_2(q_e - q_t)^2 \tag{8}$$

A linear form of the equation is:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{9}$$

where k_2 is the adsorption rate constant of second-order kinetic models in L/mg/min, q_e is equilibrium amount adsorbed at time t (mg/g) and q_t is equilibrium amount adsorbed at time $t = \infty$. The values of q_e and k_2 can be calculated by the slope and intercept plot of t/q_t versus t.

The results showed that the experimental q_e values for cadmium ions observed by using carbon nanoparticles (Pyrzynska 2010), carbon nanotubes (Hsieh & Horng 2007; Moradi *et al.* 2010; Moradi & Zare 2011) and modified multi-walled carbon nanotubes (Vukovic *et al.* 2010; Luo *et al.* 2013) have good agreement with the calculated value of saturation amount with the pseudo-second-order kinetic models. Conformity between the predicted value calculated by kinetic model and experimental value was expressed by correlation coefficient (R^2). The value of correlation coefficient (R^2) was close to 1 and the relatively high value of correlation coefficient is the more applicable model to represent the adsorption mechanism. The value of correlation coefficients (R^2) of the pseudo-first-order model were slightly less than the pseudo-second-order model for most of the carbon-based nanosorbents which indicates that the kinetic model is best explained by the pseudo-second-order model rather than the pseudo-first-order model. This indicates that adsorption of cadmium onto carbon-based nanosorbents may be explained by chemi-sorption mechanism which involves the valence forces through exchange or sharing of electrons between nanosorbents and cadmium ions.

In addition, initially at higher concentration the rate controlling step may be either the pore diffusion, boundary diffusion or the intra-particle diffusion of the cadmium

ions on the surface of carbon-based nanosorbents (Velicko-vic *et al.* 2013). The slowest of the three steps controls the overall rate of the method. The equilibrium amount adsorbed on carbon-based nanosorbents is now a function of half time ($t^{1/2}$) rather than time (t) to show the diffusion mechanism suggested by Weber and Morries as follows:

$$q_t = k_{ip}t^{1/2} + C \tag{10}$$

where k_{ip} is the intra-particle diffusion rate constant (mg/g min½) and C (mg/g) is a constant representing the film thickness.

For all reviewed carbon-based nanosorbents, the kinetic data were fitted to pseudo-first-order and intra-particle diffusion models for an initial period of the first reaction step only. However, there was better correlation to the pseudo-second-order model over a long period of time for most of the systems studied (Hsieh & Horng 2007; Moradi *et al.* 2010; Pyrzynska 2010; Vukovic *et al.* 2010; Moradi & Zare 2011; Luo *et al.* 2013).

CONCLUSION

The remarkable physical and chemical properties of carbon-based nanomaterials make these materials excellent candidates for waste water treatment. The aim of this review is to compare the maximum sorption capacity for Cd^{2+} ions by carbon-based nanomaterials from aqueous solutions. However, the comparison of maximum sorption capacity for Cd^{2+} is restricted by several parameters, such as characteristics of sorbents prepared in a similar way with similar properties, i.e., surface area, surface total active sites, surface acidity, point of zero charge and also the solution properties such as pH of solution, time of contact of solution, initial metal ions concentration, etc. In conclusion, adsorption capacity of the reviewed carbon-based nanosorbents at pH 5.0–7.5 follows the following order: modified or dispersed MWCNTs > graphene oxide > SWCNT-COOH > SWCNTs > oxidised-CNT > MWCNTs > CNTs. The removal capacity of functionalized carbon nanotubes was found to be higher than the non-functionalized carbon nanotubes. Nanofloral clusters of carbon nanotubes over alumina (NFC-CNT) were found to be the best carbon-based nanomaterial for

removal of cadmium ions from water at pH 7.5. Modification or dispersion of CNTs can considerably improve the adsorption capacity by providing more active binding sites. The amount of the contaminant cadmium that binds to the modified or dispersed MWCNTs is much higher than the AC due to π-π electron-donor acceptor properties of the modified or dispersed MWCNTs. Removal of cadmium from water takes place mainly by monolayer coverage on the adsorbent surface adopted Langmuir isotherm with great value of regression coefficient. The identified knowledge gaps are unavailability of systematic studies including similar preparation method, purity, size and surface areas of carbon-based nanomaterials. Most of the research is still based on laboratory scale only, therefore how to utilize all these nanomaterials for industrial application is still a challenging interest. It is also necessary to study the potential health risks and environmental impacts of carbon-based nanomaterials before their widespread use in different applied fields.

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