

Functionalization of acidified multi-walled carbon nanotubes for removal of heavy metals in aqueous solutions

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Abstract Water pollution is a worldwide issue for the environment and human society. Removal of various pollutants including heavy metals from the environment is a big challenge. Techniques of adsorption are usually simple and work effectively. In the current study, MWCNTs were prepared by chemical vapor deposition (CVD) of acetylene at 600 °C. Fe–Co/CaCO₃ catalyst/support was prepared by wet impregnation method. The crystal size of the catalyst was identified using XRD. Acidified functionalized multi-walled carbon nanotubes (MWCNT) were produced from oxidation of multi-walled carbon nanotubes by mixture of H₂O₂ + HNO₃ in a ratio of 1:3 (v/v) at 25 °C. The structure and purity of synthesized functionalized CNTs were examined by TEM, N₂-BET method and thermogravimetric analysis. The functional groups produced at CNTs surface were investigated using FTIR spectroscopy. Acidified functionalized MWCNTs with a high surface area of 194 m²g^{−1} and porous structure (17.19 nm) were used for water treatment from harmful cations (Pb²⁺, Cu²⁺, Ni²⁺ and Cd²⁺), single cation solutions and quaternary solution at different pH values and different times. The results were interesting because in single solutions the catalyst removed Pb²⁺, Ni²⁺, Cu²⁺ and Cd²⁺ with percentages of 93, 83, 78 and 15%, respectively, in 6 h. While in quaternary

solution, adsorption was more complex and the order of the adsorbed metals was as following: Pb²⁺ (aq) > Cu²⁺ (aq) > Cd²⁺ (aq) > Ni²⁺ (aq).

Keywords Carbon nanotubes · Chemical vapor deposition · Functionalization · Adsorption

Introduction

Heavy metals are the most important pollutants in water due to their strong toxicity to plants, animals and human beings. The most heavy metals in polluted waters include Hg, Pb, Ag, Cu, Cd, Cr, Zn, Ni, Co and Mn [1]. The heavy metals cannot be degraded or destroyed as they tend to bioaccumulate in food chains. Moreover, their natural process of mineralization is very slow. Many methods are used for removing them from polluted water. The best way to get rid of these heavy metals is by immobilization of good sorbents in solutions leading to adsorption of these heavy metals on the sorbents. Many adsorbents are used for that purpose, such as activated carbon (AC) [2–4], fly ash [5], chitin [6], activated carbon cloth [7] and resins [8]. Among all of these adsorbents, the carbon nanotubes, which are one of the carbon family that possess a great potential for removing many kinds of pollutants, such as dioxin from air [9], lead [4], cadmium, zinc, fluoride [10], 1,2 dichlorobenzene [11] from water.

Studies on adsorption of heavy metals with CNTs presented in the literature are limited to few examples as shown in Table 1. The poor solubility of CNTs in most solvents limits their applications. Their poor solubility in aqueous and organic solvents and limited compatibility with polymer matrices are major drawbacks, rendering these materials incapable of achieving their full potential.

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Table 1 Reported adsorption capacities of some CNT adsorbents for some metal ion

Type of CNT	Metal ion adsorbed	Adsorptivity (%)	References
CNTs	Pb ²⁺	17.44	[40]
MWCNTs	Cd ²⁺	7.4	[41]
	Mn ²⁺	4.8	
	Ni ²⁺	6.8	
MnO ₂ /CNTs	Pb ²⁺	78.7	[42]
MWCNTs	Cd ²⁺	10.8	[43]
	Cu ²⁺	24.4	
	Pb ²⁺	97.06	
CNTs/Al ₂ O ₃	Pb ²⁺	67.5	[44]
	Cu ²⁺	26.3	
	Cd ²⁺	8.8	
MWCNTs	Co ²⁺	2.77	[45]
MWCNTs	Pb ²⁺	8.7	[46]
Functionalized MWCNTs	Pb ²⁺	93 and 68	This study
	Ni ²⁺	82 and zero	
	Cu ²⁺	78 and 5	
	Cd ²⁺	15 and 4	

Hence, the functionalisation of nanotubes is extremely important, as it increases their solubility and process ability. Several modification approaches like physical, chemical or combined modifications have been exploited for their homogeneous dispersion in common solvents to improve their solubility and applications.

In the present study, MWCNTs were produced by CVD method by Fe–Co/CaCO₃ as a catalyst at 600 °C. The catalyst was characterized by XRD. Acidified functionalization of MWCNTs was done using H₂O₂ + HNO₃ in a ratio of 1:3 (v/v) at 25 °C. Functionalized MWCNTs were characterized by thermal analysis, FT-IR, SEM and TEM. Their capabilities to adsorb different heavy metals in single and quaternary aqueous solutions (Pb²⁺, Cu²⁺, Cd²⁺ and Ni²⁺) in different pH [5–9] solutions and different contact time were studied as shown in Scheme 1. Our work showed high % removal efficiency compared with previous studies as shown in Table 1. Langmuir and Freundlich isotherm models of adsorption were applied to fit the experimental data.

Experimental

Materials

Table 2 shows all materials which were used: iron nitrate, Fe (NO₃)₃·9H₂O, SDFCL, India; cobalt nitrate, Co (NO₃)₂·4H₂O, and cadmium nitrate, Cd (NO₃)₂·6H₂O, Oxford laboratory reagent, India; calcium carbonate, CaCO₃, sodium hydroxide, NaOH, PioChem Manufacturer

of Laboratory Chemicals, Egypt; hydrochloric acid HCl; hydrogen peroxide, H₂O₂; nitric acid, HNO₃. All used chemicals were of analytical reagent grade and were not more purified; besides, all solutions were prepared using bi-distilled water.

Preparation of the catalyst

The catalyst/support (Fe–Co/CaCO₃) was prepared by impregnation method [12]. In the first step, commercial CaCO₃ was milled for 10 h to decrease the crystallite size and increase the surface area (see Table 3). Iron and cobalt nitrates, (Fe(NO₃)₃·9H₂O) and (Co(NO₃)₂·6H₂O), were added to support (CaCO₃) with certain weight ratio (2.5:2.5:95), respectively. Milling was continued for another 2 h. Few drops of distilled water were added to the produced catalyst/support mix making a paste just to ensure the homogeneity. The paste was then dried overnight at 120 °C for 12 h and then ground well to obtain a fine powder of Fe–Co/CaCO₃ catalyst/support mixture [13].

Preparation and acidification of CNTs

CNT preparation and oxidized MWCNTs were prepared by catalytic chemical vapor deposition (CVD). The produced supported catalysts were stored in a sealed vessel and CNTs were synthesized over the catalyst. About 2 g of catalyst was packed in a cylindrical alumina cell. The catalyst was preheated to 600 °C in a flow of nitrogen gas (70 ml/min) for 10 min. Then acetylene gas was allowed to pass over the catalyst bed with a rate of 10 ml/min for



Scheme 1 The application of Fe–Co/CaCO₃ nanoparticles to produce MWCNTs for removing heavy metals from wastewater

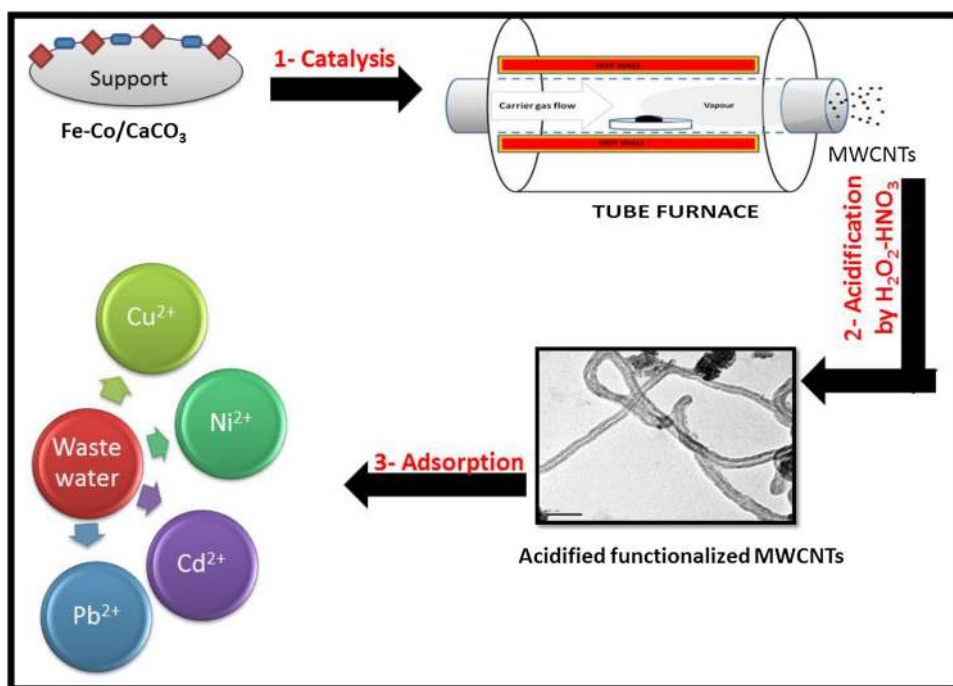


Table 2 The specifications of the chemicals used

Cobalt (II) nitrates (Co(NO ₃) ₂ ·6H ₂ O)	(Oxford Laboratory Reagent, India)
Ferric (III) nitrates (Fe(NO ₃) ₃ ·9H ₂ O)	(SDFCL, India)
Calcium carbonate powder (CaCO ₃)	(PioChem)
Acetylene gas (C ₂ H ₂) pure	(Commercial)
Nitrogen (N ₂) pure gas	(Commercial)
Nitric acid (HNO ₃) conc.	(Commercial)
Hydrogen peroxide (H ₂ O ₂)	(PioChem)
Sodium hydroxide (NaOH)	(PioChem)
Hydrochloric acid (HCl) conc.	(Commercial)
Nickl(II) nitrates (Ni(NO ₃) ₂ ·6H ₂ O)	(WINLAB, UK)
Lead (II) nitrates (Pb(NO ₃) ₂)	(WINLAB, UK)
Cadmium chloride (CdCl ₂)	(Oxford Laboratory Reagent, India)
Copper nitrate (Cu(NO ₃) ₂)	(WINLAB, UK)

Table 3 Ball milling conditions for preparing Fe–Co/CaCO₃ catalyst/support

Condition	Description
Vessel size	7.5 cm diameter
Balls diameters	Ranged from 1.11 to 1.75 cm diameter
Materials of vessels	Stainless steel
Materials of balls	Porcelain
Ball/precipitate mass ratio	8:1 mass ratio
Speed	300 rpm
Time	10 h

60 min. The acetylene gas flow was stopped and the product on the alumina cell was cooled to room temperature in a flow of nitrogen gas.

MWCNTs purification process was achieved using chemical acidified oxidation method. Approximately 0.5 g of MWCNTs was sonicated at 25 °C in 200 ml of mixture of the H₂O₂ + HNO₃ in a ratio of 1:3 (v/v). After 3 h of sonication, the acid-treated MWCNTs was diluted with 200 ml of distilled water and filtered through a filter paper with 3 µm porosity. The acid-treated MWCNTs were then washed thoroughly with distilled water until a neutral pH is reached and dried at 100 ± 0.5 °C for 3 h [14].



Adsorption experiments

Analytical grade lead nitrate, nickel nitrate, cadmium chloride and copper nitrate were employed to prepare a stock solution containing 1000 mg/l for the four metal ions, which were further diluted to the required concentrations before usage. The adsorption of all cations was studied by a batch operation at 25 ± 0.5 °C [15].

Single metal ion adsorption experiments

In single metal ion experiments, 0.05 g of acidified functionalized MWCNTs was placed in 100 ml solutions of concentration 100 mg/l. Each single cation solution was adjusted at different pH values [5–9]. If necessary, an appropriate volume of 0.1 M HNO_3 or 0.1 M NaOH solutions was used to adjust the pH of the solution. The prepared samples were shaken with an orbital shaker at a shaking speed of 200 rpm at room temperature for 6 h. Then solid/liquid phases were separated by filtration. The concentration of the different cations before and after adsorption was determined using atomic absorption spectrometry (Agilent Technologies 200 Series AA). The adsorbed amounts of metal ions onto the acidified functionalized MWCNTs were determined according to the following equations [1]:

$$Q = \frac{(C_o - C_t)}{C_o} \times 100, \quad (1)$$

where Q is the adsorptivity (%), C_o represents the initial concentration of metal ion and C_t is the concentration of metal ions in (mg/l) after adsorption at time t (min). The amount of metal ion adsorption at equilibrium q_e (mg/g) was determined by the following equation:

$$q_e = \frac{V(C_o - C_e)}{W}. \quad (2)$$

In the equation, the equilibrium adsorption capacity of adsorbent in mg (metal)/g (adsorbent) represented by q_e , C_o stands for the initial concentration of metal ions before adsorption in mg/l and C_e is the equilibrium concentration of metal ions in mg/l. The metal ion solution volume in l is represented by V , and W stands for the adsorbent weight in g [16].

Competitive adsorption experiments

To investigate the competitive adsorption of the four cations (Pb^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+}) on MWCNTs at different pH values [5–9], 0.05 g of acidified functionalized MWCNTs was added to 100 ml solution with equal initial concentrations of the four heavy metals (100 mg/l) and the experiment was completed as previously described.

The same experimental conditions were carried out to study the effect of time by shaking the solution for 10 h and the filtrate concentration was measured every 2 h by atomic adsorption spectroscopy. The absorptivity percentage was calculated by equation [1].

Characterization

(Fe–Co/ CaCO_3) was characterized by X-ray diffraction technique using JSX-60P JEOL diffractometer. The morphology of acidified functionalized MWCNTs was investigated by transmission electron microscope (JEOL JEM-1230). The physical properties of sorbents were determined by nitrogen adsorption at 77 K using ASAP-2010 surface area analyzers. N_2 adsorption isotherms were measured at a relative pressure range 0.0001–0.99. The adsorption data were then employed to determine surface area using Brunauer–Emmett–Teller equation and pore size distribution (including average pore diameter and pore volume) using Barrett–Johner–Halenda equation. The functional groups on the surface sites of MWCNTs were detected by a Fourier transform infrared spectrum (model FT/IR-6100 type A). The carbon content of the sorbents was determined by a thermogravimetric analyzer (model Labsys TG-DSC 50H). Heavy metals' concentrations were determined by atomic adsorption spectrometer (model ZEISS-AA55, Germany).

Results and discussion

Characterizations of synthesized materials

Figure 1 shows the XRD patterns of the catalyst (Fe–Co/ CaCO_3) used for the preparation of MWCNTs by CVD method and the resulting peaks indicate the presence of the following phases (1: CaCO_3 , 2: Fe_2O_3 , 3: CoO). CaCO_3 is a non-porous support material by which the formation of amorphous carbon is suppressed during nanotubes growth and, therefore, selective formation of CNTs is promoted. Purification can be achieved in one step in which both metallic particles and catalyst support can be dissolved in $\text{H}_2\text{O}_2 + \text{HNO}_3$. After purification, CNTs were produced with high yield, high purity and less damage of graphitic walls.

Figure 2a, b shows the TEM images of acidified functionalized MWCNTs. The tubes are highly long (~ 3 μm) and curved with some open tips. The images show clearly a hollow inner tube with a diameter of 3 nm and an outer diameter of 19 nm. Catalyst nanoparticles were encapsulated at the ends of nanotubes, confirming a tip-growth mechanism [17]. The mixed oxide particles seem to be necessary for the growth because they are often found at



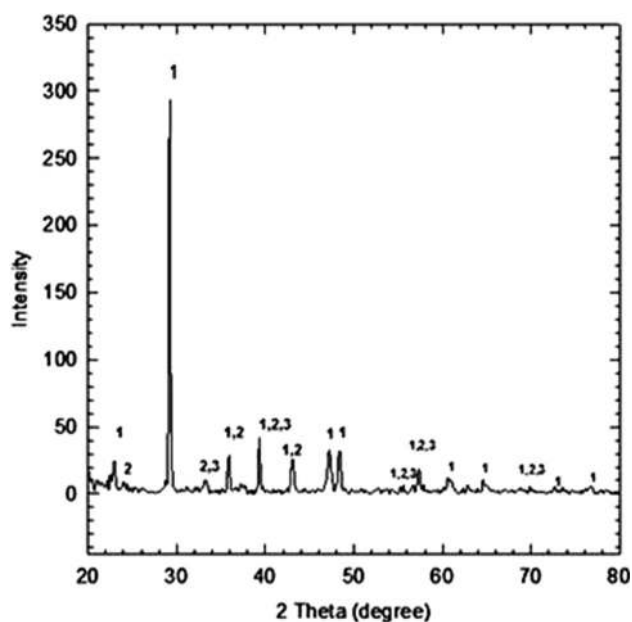


Fig. 1 X-ray diffraction patterns for Fe–Co/CaCO₃ catalyst/support, Fe₂O₃ [1], CoO [2] supported on CaCO₃ [3]

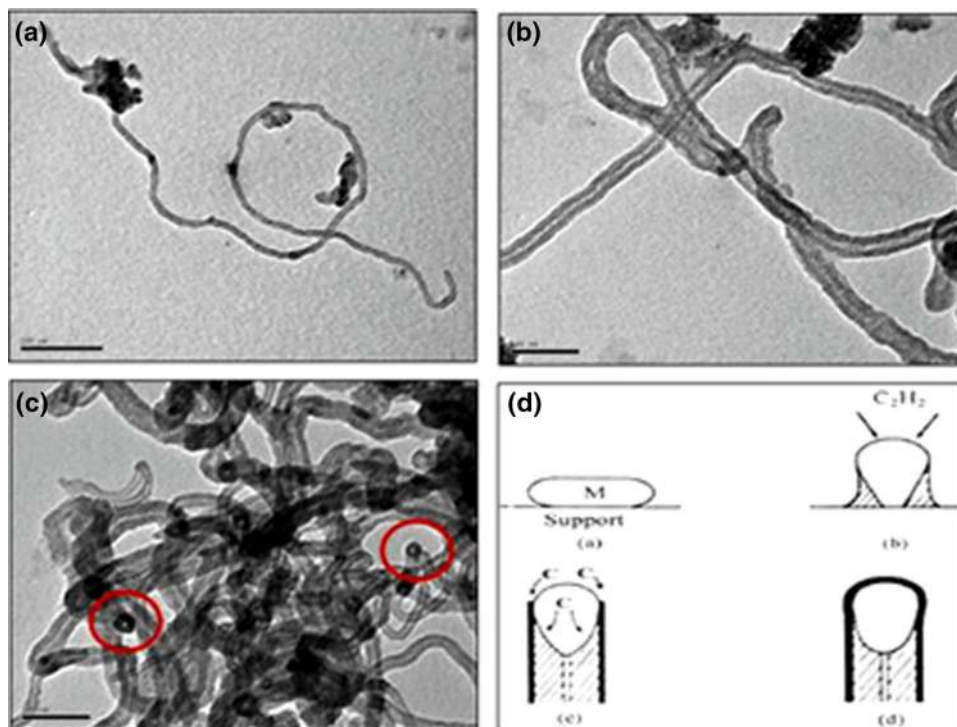
the tip inside the nanotube or also somewhere else in the middle of the tube as shown in Fig. 2c (marked with black spot). It is supposed that acetylene decomposes at 600 °C on the top of a supported catalyst as shown in Fig. 2d. The dissolved carbon diffuses in the catalyst, precipitates on the rear side and forms nanotubes. The carbon diffuses through

the catalyst due to a thermal gradient formed by the heat release of the exothermic decomposition of acetylene [18].

FTIR spectra of acidified functionalized MWCNTs are shown in Fig. 3, indicating that the acid treatment generated functional groups on the surface of MWCNTs. The corresponding band close to 3438 cm⁻¹ could be attributed to free hydroxyl groups on acidified functionalized MWCNTs surface. On the other hand, the characterized peak that appeared at 2925 cm⁻¹ could be attributed to the stretching vibration of C–H, while the peak at 1704 cm⁻¹ could be attributed to carboxyl groups. The peak observed at 1628 cm⁻¹ is the C=C stretch of the MWCNTs, while asymmetric carboxylate anions' stretch mode was shown at 1575 cm⁻¹. The peak located at 1462 cm⁻¹ could be attributed to carbonyl groups [19]. The absorptions at 1384 cm⁻¹ were associated with symmetric COO⁻ stretching [2, 20, 21]. These produced functional groups abundantly on the external and internal surfaces of acidified functionalized MWCNTs, which can provide numerous chemical sorption sites and thus increase the ion exchange capacity for the metal ion, in other words, the hydrophilic properties of these functional groups improve the dispersity of MWCNTs in aqueous solution.

To give a further insight into the specific surface area and porosity of the as-prepared acidified functionalized MWCNTs, the BET surface area, average pore diameter and pore volume were calculated using the BJH method as shown in Table 4. The specific surface area value of the

Fig. 2 TEM images of **a**, **b** acidified functionalized MWCNTs, **c** MWCNTs after adsorption of Pb(II) and **d** growth model of vapor grown carbon nanotubes



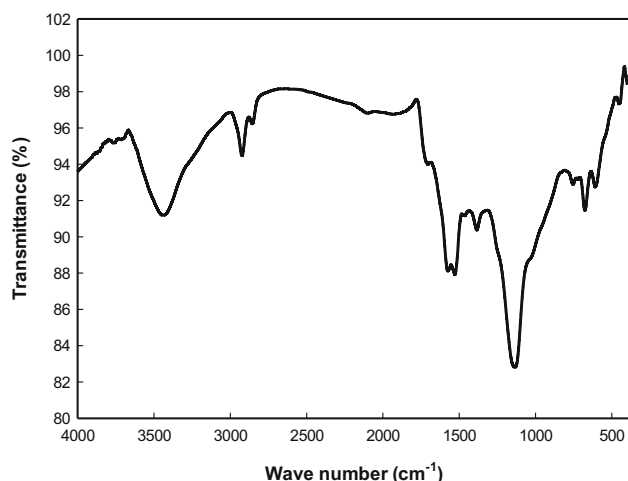


Fig. 3 FT-IR spectra of acidified functionalized MWCNTs

acidified functionalized MWCNTs is found to be $194.36 \text{ m}^2/\text{g}$, which is greater than that of prepared MWCNTs adsorbent [17], and thus adsorption capability and adsorption active sites will be increased. Removing amorphous carbon, carbon black and carbon nanoparticles introduced by CVD method leads to better dispersion of CNTs, breaks the inner tube spaces and even opens the tips partially. Figure 4 presents the adsorption–desorption isotherms of N_2 on the acidified functionalized MWCNTs, and it is apparent from the adsorption and desorption curves that it exhibits a type II shape. It was observed that there is a small closed adsorption–desorption hysteresis loop with relative pressure above 0.4, which is suggested to be due to mesopores and capillary condensation [22].

Figure 5 reveals the TGA results of acidified functionalized MWCNTs, which show temperature range for weight loss and exhibit two main weight loss regions. The first weight loss region ($\sim 10\%$) can be attributed to the loss of various kinds of functional groups that were produced on the surface of MWCNTs due to acidification treatment. The second region ($\sim 35\%$) may be attributed to the gasification of MWCNTs at which its decomposition begins at 405°C and ends at 610°C .

Table 4 Surface area measurements for MWCNTs

Surface area (m^2/g)	194.4
Total pore volume (cc/g)	0.0835
Average pore diameter (nm)	17.19
Micro pore volume (cc/g)	0.17

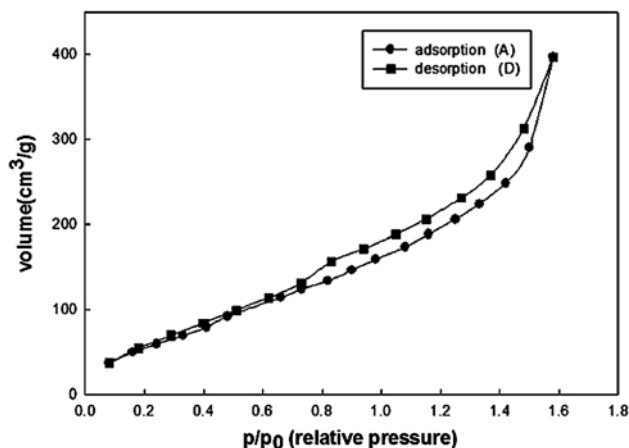


Fig. 4 N_2 adsorption–desorption isotherms of acidified functionalized MWCNTs

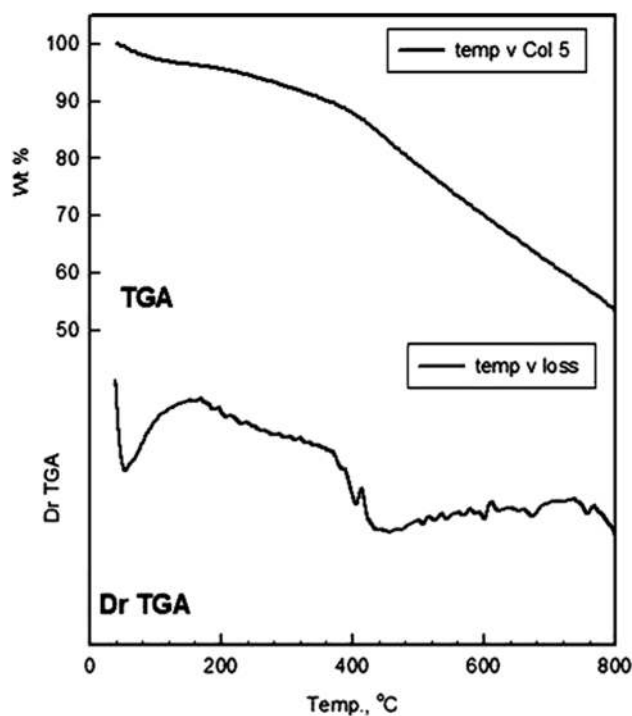


Fig. 5 TGA of acidified functionalized MWCNTs

Adsorption analysis of different metal ions (Pb^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+})

Adsorption isotherm of single metal ions solutions

The adsorption equilibrium isotherm is important for describing how the adsorbate molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state. The adsorption isotherms of single cation solutions of Pb^{2+} , Cu^{2+} , Cd^{2+} and Ni^{2+} on the acidified functionalized MWCNTs are shown in



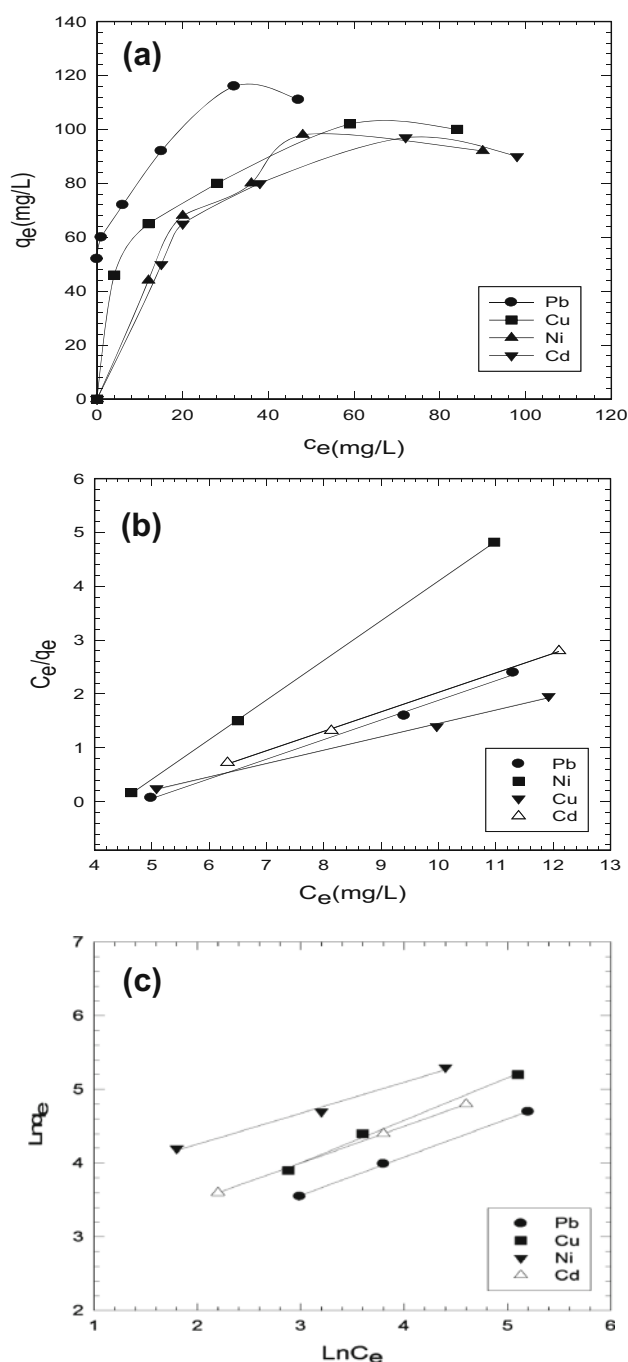


Fig. 6 Langmuir (a) and Freundlich (b) isotherms for adsorption of Pb^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+} onto acidified functionalized MWCNTs

Fig. 6a. Equilibrium uptake increased with heavy metal concentrations. This is a result of the increase in the driving force from the concentration gradient. In the same conditions, if the concentrations of heavy metals in solutions are higher, the active sites of the CNTs are surrounded by many more heavy metal ions and the process of adsorption would be carried out sufficiently. The experimental data for single component solutions containing Pb^{2+} , Cu^{2+} , Cd^{2+}

and Ni^{2+} ions could be approximated by Langmuir and Freundlich isotherm models.

The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer. The Langmuir isotherm [23] is represented by the following linear equation [3]:

$$\frac{C_e}{q_e} = \frac{1}{(q_0 K_L)} + \frac{1}{(q_0)} C_e, \quad (3)$$

where C_e (mg/l) is the equilibrium concentration, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbate, and q_0 and K_L are the Langmuir constants related to the adsorption capacity and the rate of adsorption, respectively. When C_e/q_e was plotted against C_e , a straight line with a slope of $1/q_0$ was obtained (Fig. 6b), indicating that the adsorption of the four heavy metals (Pb^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+}) on acidified functionalized MWCNTs follows the Langmuir isotherm. The Langmuir constants K_L and q_0 were calculated from this isotherm and their values are listed in Table 3. Another important parameter, R_L , called the separation factor or the equilibrium parameter, is evaluated in this study and determined from the following relation [4, 24]:

$$R_L = \frac{1}{[1 + K_L C_0]}, \quad (4)$$

where K_L is the Langmuir constant (l/mg) and C_0 (mg/l) is the highest metal ion concentration. The value of R_L indicates whether adsorption onto the MWCNTs will be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values for Pb^{2+} , Cu^{2+} , Cd^{2+} and Ni^{2+} were less than 1 and greater than zero indicating favorable adsorption (Table 5).

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. The linear form of the Freundlich equation [5] is

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e, \quad (5)$$

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of the four metal ions. K_F and n are Freundlich constants, where K_F ($\text{mg/g (l/mg)}^{1/n}$) is the adsorption capacity of the adsorbent and n gives an indication of how favorable the adsorption process is. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity. The surface becomes more heterogeneous as its value gets closer to 0 [25]. Figure 9c shows straight lines with slope $1/n$. The adsorption of Pb^{2+} , Cu^{2+} , Cd^{2+} and Ni^{2+} also follows the Freundlich isotherm. Accordingly (Fig. 6c) Freundlich



Table 5 Isotherm parameters for removal of Pb^{2+} , Cu^{2+} , Cd^{2+} and Ni^{2+} by acidified MWCNTs

Isotherms	Parameters	Heavy metal ions			
		Pb^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}
Langmuir	q_o (mg/g)	166	123	95	101
	K_L (l/mg)	0.485	0.384	0.061	0.560
	R_L	0.017	0.19	0.020	0.018
	R^2	0.997	0.997	0.998	0.999
Freundlich	K_F (mg/g (l/mg) $^{1/n}$)	42.23	15.12	37.58	31.96
	N	3.89	2.065	3.012	2.95
	R^2	0.999	0.995	0.990	0.971

constants (K_F and n) were calculated and are listed in Table 5.

Effect of contact time in Pb^{2+} solution

The importance of contact time comes from the need for identification of the possible rapidness of binding and removal processes of the tested metal ions by the synthesized adsorbents and obtaining the optimum time for complete removal of target metal ion. Figure 7 illustrates the effect of contact time on the adsorption of Pb^{2+} ions onto acidified MWCNTs at initial concentration of 100 mg/l and pH 9. In agreement with previous studies [26, 27] there is a significant increase in the adsorption capacity of Pb^{2+} ions as the contact time increases. The analysis of batch adsorption of metal ions was carried out in 2 h and the concentration of each sample was measured by atomic absorption spectroscopy; first after 2 h, the adsorption percentage reached 84%, which may be due to the fact that the initial adsorbent sites were vacant and the solute concentration gradient was high. Later, equilibrium

was achieved at a time period ranging from 6 to 8 h and the adsorption percentage reached to 89.8 and 90.2%, respectively. Finally, a sharp increase after 8 h occurred and complete adsorption was achieved at 10 h as adsorption percentage reached 99.6% and was considered the optimum condition.

Effect of MWCNTs dose

To clarify the function of MWCNTs on adsorption capacity of lead ions, eight weights of MWCNTs (0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5 and 0.6 g) were used to adsorb Pb^{2+} ions from aqueous solution as shown in Fig. 8. After shaking time, adsorption percentage (%) of lead ions onto MWCNTs reached sharply 13.63, 23.55, 39.13, 50.96, 72.23, 73.1, 73 and 72.9 as the CNTs weight increased from 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5 and 0.6 g, respectively. Therefore, the increase of MWCNTs can obviously increase the adsorption percent of Pb^{2+} [28–30]. Furthermore, the increase in percentage of removed lead ions with an adsorbent dosage can be attributed to an increase in the adsorbent surface which increased the availability of

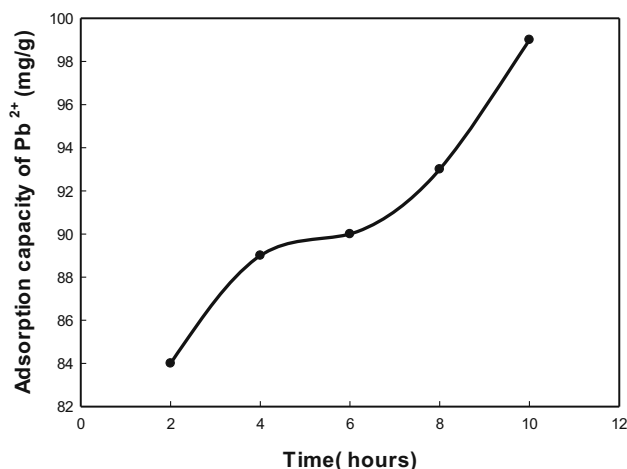


Fig. 7 The effect of contact time on adsorption of Pb^{2+} ions for acidified functionalized MWCNTs

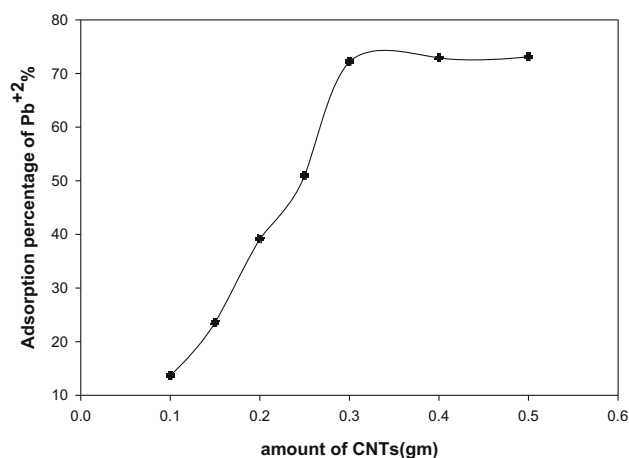


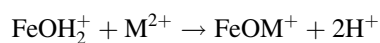
Fig. 8 Shows the effect of MWCNTs dose on the adsorption of Pb^{2+}



adsorption sites; while further increase in CNT dose did not show any increase in adsorption percentage [31]. As indicated from data, there is no more adsorption up to 0.5 g of used CNTs.

Effect of different pH for different metal ions (Pb^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+})

Previous studies [32] showed that the pH of solution is the most important variable governing heavy metal ions adsorption. Figure 9 shows that at low pH value, the surface of the adsorbent would be closely associated with hydronium ions (H_3O^+) and hold mainly protonated sites. As a result, the surface maintains a net positive charge. So it hinders the access of the metal ions to the surface functional group. Consequently, the percentage removal of metal ions decreases as the pH values decreased. The positive charge on adsorbent surface, however, gradually decreases as pH increases, thus reducing the electrical repulsion between sorbing surface and cations. Moreover, lower H concentration also favors cation sorption by mass action. For example, the adsorption of bivalent cations such as M^{2+} on iron oxide can be written as:



Lowering H^+ concentration will drive this reaction toward the right-hand side and favor the sorption of M^{2+} by increasing pH [33]. That shows good agreement with Surface Complex Formation Theory (SCF), which states the following: by increasing pH, the competition for adsorption sites between protons and metal species decreases [19]. As a result, by increasing pH value there are more and more attractive forces due to the presence of surface negative charges.

Effect of different metal ions on the adsorption of Pb^{2+} at different pH

In a quaternary aqueous solution containing equal concentrations of Pb^{2+} , Cu^{2+} , Cd^{2+} and Ni^{2+} using serial pH values [5–9], the effect of pH was presented in Fig. 10 which shows that as the pH increase, the adsorption capacities for Pb^{2+} , Cu^{2+} and Cd^{2+} increase, while Ni^{2+} did not show any adsorption capacity in all pH values. The maximum adsorption capacities reached at pH 9 for three metals Pb^{2+} , Cu^{2+} and Cd^{2+} . The experimental data indicate that the adsorption affinities for the four metals take the sequence, $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$, which agrees with Li et al. [34]

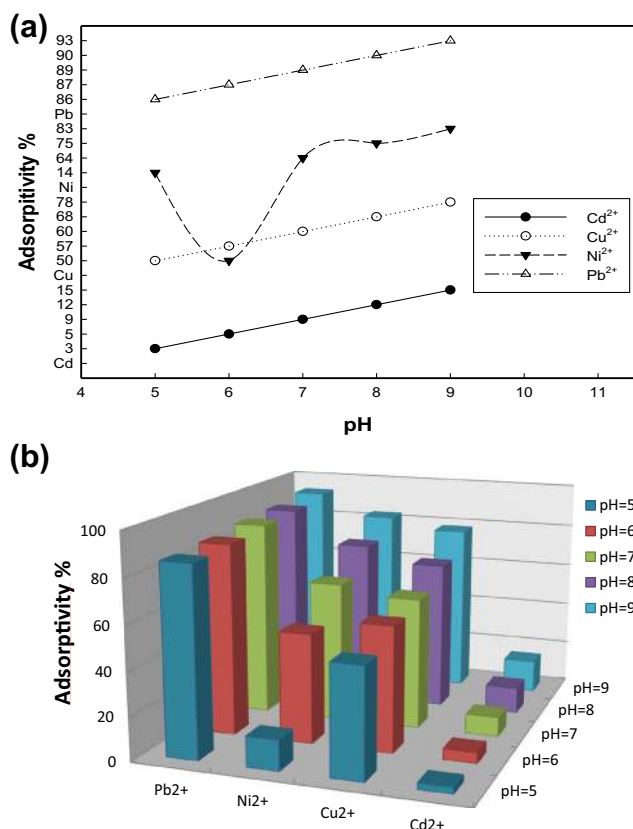


Fig. 9 The effect of different pH [5–9] on the adsorption uptake of metals Pb^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+} , in single solution

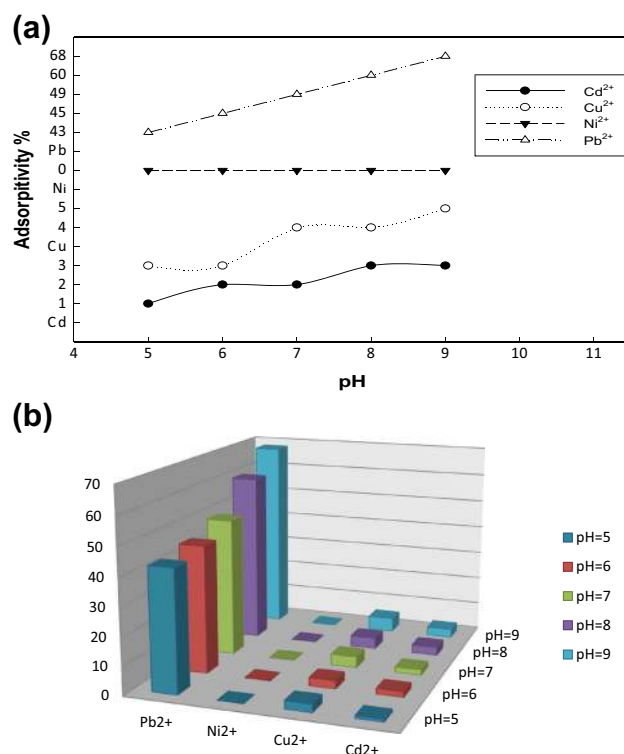


Fig. 10 The effect of different pH [5–9] on the adsorption uptake of metals Pb^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+} , in multi-solution



Ni^{2+} has no ability to compete the other three metal ions as it is considered to be the most weakly adsorbed species. Many studies attributed the behavior of the multi-component systems to the CNT adsorption sites [34–36] and found that Pb^{2+} and Cu^{2+} both have higher affinities more than Cd^{2+} and Ni^{2+} . The competitive adsorption may be related to ion exchange and electrochemical properties of the cations. The higher the complex redox properties and ion exchange processes, the higher is the polarizability of the ion, the smaller is the value of N/R_H (N is the number of water of hydration and R_H is the hydrated radius) and greater the affinity between the ions and functional groups [37]. However, there is no consensus among researchers regarding the competitive adsorption of metal ions [38, 39].

Conclusions

Fe–Co/ CaCO_3 catalyst/support was successfully prepared by wet impregnation method and characterized by XRD. The MWCNTs was synthesized in a homogeneous form by chemical vapor deposition (CVD) of acetylene on the catalyst surface at 600 °C with high density and high purity. The synthesized MWCNTs were purified by a mixture of $\text{H}_2\text{O}_2 + \text{HNO}_3$ in a ratio of 1:3 (v/v) at 25 °C leading to formation of functional groups on its surface. The functionalized MWCNTs were characterized using FTIR, TEM, BET and TGA. FTIR spectra of functionalized MWCNTs confirmed the presence of several functional groups. These produced functional groups can provide numerous chemical sorption sites on MWCNTs surface. From single and quaternary solutions of the four heavy metals (Pb^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+}), the following conclusions could be obtained:

1. The adsorption of Pb^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+} in both single and quaternary solutions increases with increase of the solution pH.
2. The large adsorption capacity of acidified MWCNTs for the metals is mainly due to the oxygenous functional groups on its surface which could react with metals to form salt or complex deposits on the surface of MWCNTs.
3. The removal process of the metals is related to the surface chemistry of oxidized MWCNTs.

The adsorption experimental results of these heavy metals are in a good correspondence with the Langmuir and Freundlich isotherms.

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