

Multi Walled Carbon Nano Tubes and Ferric Oxide Nanomaterial as Adsorbents for Removal of Some Heavy Metals from Contaminated Water (Ground and Industrial Waste Water)

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Abstract

The aim of this study was to find out an available and low cost material to reach the permissible levels of the heavy metals Mn^{2+} , Fe^{2+} and Pb^{2+} in the contaminated water (ground and industrial waste water) taken from Kaha, El-Qulayoubia Governorate using multi walled carbon nanotubes (MWCNTs) prepared from chemical vapor deposition (CVD) and ferric oxide nanoparticle (Fe_2O_3) with potassium permanganate ($KMnO_4$). Also, it involved the characterization of MWCNTs and Fe_2O_3 nanoparticle and determine the optimal conditions for the treatment. The effects of MWCNTs, Fe_2O_3 nanoparticle and $KMnO_4$ on removal of manganese, iron and lead from contaminated water was the main target of this investigation. In this work the highest initial Mn^{2+} , Fe^{2+} and Pb^{2+} ion concentrations (C_0) were found to be 3.42, 4.2 and 23 mg/L, respectively, were treated with multiwall carbon nanotubes, ferric oxide and potassium permanganate. MWCNTs was of 20-30 nm outer diameter, 5-10 nm internal diameter, surface area of 207.13 m^2/g , carbon content 90.05%, oxygen content 6.9% and purity above 87%, while, Ferric oxide particle size averaged 5-10 nm, ferric content 44.64%, oxygen content 41.67% and carbon content 10.97%.

The optimum conditions for removing Mn^{2+} and Fe^{2+} ion from the contaminated water with MWCNTs/ $KMnO_4$, were a pH of 7.5, volume $KMnO_4$ 0.25 mL, adsorbent weight of 0.05 g and a contact time of 90 min. The optimum conditions for removing Pb^{2+} ion with Fe_2O_3 / $KMnO_4$ were a pH at 6.7, adsorbent weight 0.06 g, volume of $KMnO_4$ 1.25 mL and a contact time of 120 min.

Key words: Carbon nano tubes - Ferric oxide - Heavy metal - Contaminated water

Introduction

Heavy metals are natural components of the Earth's crust. The metal ion enter our bodies via air, drinking water and food. Some heavy metals e.g. manganese, iron and zinc are essential to maintain the metabolism of the human body but at higher concentrations may cause poisoning, leading to desfunction of the reproductive system, liver, kidney and central nervous system (Brent, 2006). Heavy metals such as lead, arsenic, cadmium and mercury are introduced to the environment by different human activities and deposit slowly in the surrounding water and soil (Gupta *et al.*, 2015).

Carbon nanotubes (CNTs) are materials related to both graphite and fullerenes. Multiwall Carbon Nano Tubes (MWCNTs) have unique properties, such as high thermal and electrical conductivity, high strength, and special adsorption properties. The removal of inorganic and organic pollutants from waste water by CNTs has been studied by several investigations (Iijima, 1991).

Wang *et al.* (2007) studied the adsorption of Pb (II) using acidified MWCNTs and found that the exogenous functional groups on MWCNTs play an important role in Pb (II) adsorption through forming chemical complex adsorption, which accounts for 75.3% of all the Pb (II) adsorption capacity.

The maximum iron and manganese contents varied from 30 to 50 and 1.5 to 4.5 mg/L, respectively. Under the best conditions, simple coagulation (flocculation) was allowed to obtain iron removal yields of 18 to 75%. Manganese was eliminated between 8 and 24%. Pre-oxidation with 2.5 mg/L potassium permanganate allowed attaining about 99% elimination of iron at pH 6.5 and about 95% of manganese at a pH of 8.5 in underground water (Roccaro *et al.* 2007).

The removal of lead (Pb^{2+}) from polluted water by modification Carbon Nano Tubes (M-CNTs) was maximum under fixed conditions of pH, (7.0), contact time (2 h) and agitation speed at 150 rpm. By using M-CNTs, the removal reached up to 100% by adding 10 mg of the adsorbent, while, by using R-CNTs (no modification), the maximum removal percentage of lead was 100% after adding 80 mg of adsorbent (Atieh *et al.* 2010).

Nassar (2012) studied the removal of Pb^{2+} ion from aqueous solution by Fe_3O_4 nanoadsorbent. The maximum adsorption capacity of Pb^{2+} was found to be 36 mg/g under contact time of 30 min.

Ganesan *et al.* (2013) applied a batch adsorption process to investigate the removal of manganese from aqueous solution by oxidized Multi Walled Carbon NanoTubes (MWCNTs) and found that the removal

percentage of Mn^{2+} ion reached 96.82% and equilibrium was achieved within 354 min.

Elsehly et al. (2015) studied the removal efficiency of (Fe^{2+}) ion by oxidized MWCNTs (O-CNTs) and found that the removal efficiency of iron could reach 52% for initial concentration of 50 mg/L.

Abd-Elhakeem et al. (2015) studied the effect of chitosan nanoparticles on removal of heavy metal ions Mn^{2+} , Fe^{2+} , Zn^{2+} and Cu^{2+} and found that the optimum conditions were 2 g/L dose of the nanoparticles, contact time 30 min and pH value at 7 for initial concentration of 20 mg/L of each metal ion. Also the removal percentages were 80.8% for Mn^{2+} , 99.94% for Fe^{2+} , 90.49% for Zn^{2+} and 95.93 % for Cu^{2+} ions.

Materials and Methods

Ground water samples were obtained from Kaha City, in El-Kalyoubia Governorate during the period extending from 2/2016 to 6/2017.

The industrial waste water samples were obtained from Kaha Company of the Chemical Industries, Battery Department during the period extending from 6/2016 to 6/2017. These samples were collected and kept in polyethylene plastic bottles ($4^{\circ}C$).

All the reagents used for analyses and the other chemicals used in this study were obtained, from El-Gomhorya and Sigma Chemical Companies.

Multi Wall Carbon Nanotubes (MWCNTs) and ferric oxide nanoparticles were obtained from Since Technology Center of Excellence. Activation of MWCNTs with nitric acid and sulfuric acid was carried out according to the methods described by **Chiang et al. (2011)**.

Characterization of the nano-adsorbents:

Scanning electron microscopy (SEM) was used to investigate the surface morphology, it revealed the uniformity of dispersion of the nanoparticles (**Goldstein et al., 2003**). Transmission electron microscopy (TEM) the average size and diameter of the nanoparticles (MWCNTs) were obtained from the TEM image. TEM was performed by dipping holey carbon and grid into a colloidal suspension of the MWCNTs. TEM was employed to observe the loading state of the Nano composites and the surface CNTs coated or embedded with nanoparticles (**Cowley, 1988**). Fourier transform infrared spectroscopy (FTIR) can provide information on the surface functional groups according to **Lix et al. (2003)**. X-ray diffraction spectroscopy (XRD) was used to calculate the average crystallite size (D) by Scherrer's equation (**Scherrer et al., 1918**). Energy dispersive X-ray (EDX) was used to confirm the percentage, and the atomic ratio of components on the surface of the Nano composite, (**Amais, 2007**). Thermogravimetric analysis (TGA) curve was used to measure the

degradation temperature of CNTs. Higher degradation temperature are always associated with purer, less defective and highly crystalline CNTs (**Sivaram et al., 2004**). The common method used to measure the surface area of the used solid adsorbents was the Brunauer-Emmett-Teller (BET) method (**Brunauer, 1938**).

Batch model adsorption experiment:

Factors affecting the adsorption process such as, pH, adsorbent weight, suitable volume of $KMnO_4$, and contact time were studied. In all cases, both the ground water and industrial waste water were mixed individually with 0.05 g of the nano adsorbents was added to 0.05 L of the sample each. The bottles were shaken using a thermo stated shaker at a speed of 210 rpm at room temperature. The pH of each sample was at the range 2-8 using 0.1 M HCl or 0.1 M NaOH. After equilibrium times of 15, 30, 45, 60, 75, 90 and 120 min the adsorbent was filtered and the filtrates were analyzed for Mn^{2+} and Fe^{2+} or Pb^{2+} using Atomic Absorption Spectrophotometer, type (Thermo-S4AA system-England).

Statistical analysis:

All results were statistically evaluated by one-way analysis of variance (ANOVA) and using the statistical software SPSS 22.0 (SPSS Ltd., Surrey, UK). Ratio values were not arcsine transformed before statistical analysis. Data were treated as complete randomized design according to **Steel et al. (1997)**. Multiple comparisons were carried out applying LSD.

Results and Discussion

Physicochemical properties and initial concentrations levels of manganese, irons and lead under investigation before treatment:

The obtained results are presented in Table (1). The initial concentrations of the studied heavy metals in the ground water were higher than the permissible levels reported by the Egyptian Environmental Affairs Agency [according to resolution No. (458/2007)], where the permissible limits of Mn^{2+} , and Fe^{2+} were 0.4 and 0.3 mg/L, respectively, while, the values of the initial concentrations of the above mentioned metals in Kaha City were found to be 3.42 and 4.2 mg/L, respectively. Also, the higher turbidity, electrical conductivity, total hardness (Ca + Mg) were 9.28 NTU, 1295 μ -siemens and 648 mg/L respectively. On the other hand, the lead ion concentration (23 mg/L) was higher than the permissible level according to the Egyptian Environmental Affairs Agency (EEAA), Laws 48/1982, 9/1989 or 4/1994 which is 0.05, 1 or 0.05 mg /L respectively. These results are in agreement with those reported by **Badawy et al. (2011)**.

Table 1. Physicochemical properties and concentration levels of Mn^{2+} , Fe^{2+} and Pb^{2+} under investigation before treatment.

Parameter	Value	Permissible level according to resolution No. (458/2007) and law4/1994
pH	7.7	6.5 - 8.5
Turbidity	9.28*	1 NTU
Electrical conductivity (EC)	1295 *	up to 1000 μ Siemens
Total soluble salts (TSS)	986	1000 mg/L
Total hardness (Ca + Mg)	648*	500 mg/L
Cl ⁻	122.7	250 mg/L
SO ₄ ²⁻	160.5	250 mg/L
Mn ²⁺	3.42*	0.4 mg/L
Fe ²⁺	4.2*	0.3mg/L
Pb ²⁺	23	0.5 mg/L

*: mean value more than permissible level

Characterization of MWCNTs, ferric oxide nano particles (Fe_2O_3 N.P.)

Defect and binding regions could in the SEM images (Fig. 1a, b). The sidewalls of the MWCNTs are considerably defected. The destructive effect is

relative to oxidation agent to the outer layers of the walls of CNTs which have been linked with function group such as OH or COOH. These results are in agreement with those reported by Shoushan *et al.* (1999).

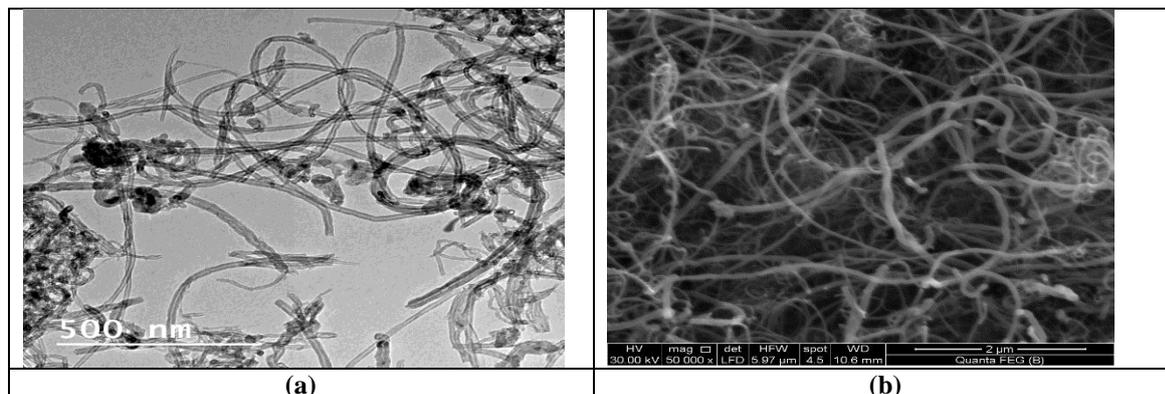


Fig. (1): SEM images (a and b) of MWCNTs

Also, TEM microscopic investigation showed a typical oxidized multi walled carbon nano tubes (O-CNTs) . Fig. 2 with inner tube diameter of about 5-10

nm, outer tube diameter of about 20-30 nm and length up to 5 μ m.

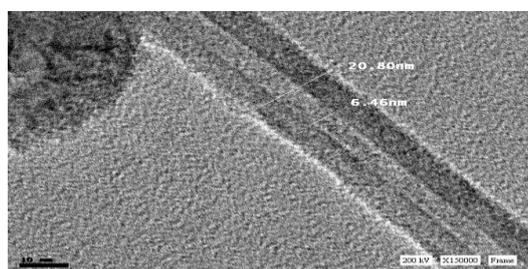


Fig. (2): TEM image of oxidized MWCNTs (O-CNTs)

FTIR spectra of functionalized CNTs are shown in Fig. (3), the peaks which are identified at 1632.72 cm^{-1} , 2921.52 and 3437.48 cm^{-1} are due to the carbonyl group (C=O), carbon hydrogen bond (C-H) and

hydroxyl group (OH), respectively. The obtained data are similar to those reported by Martinez *et al.*(2003) and Chiang *et al.*(2011).

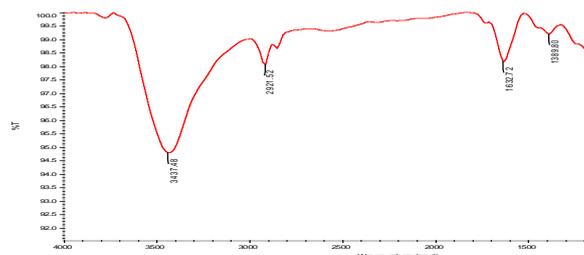


Fig. (3): Fourier transformed infrared (FTIR) spectra of (O-MWCNTs)

Fig. (4) Shows X-ray diffraction pattern of oxidized MWCNTs. The pattern shows crystalline intense peak at $2\theta = 26.6^\circ$, compared to the normal

graphite at $2\theta = 26.5^\circ$. These results are in agreement with those reported by **Zhang *et al.* (2002)** and **Hyung and Kim (2008)**.

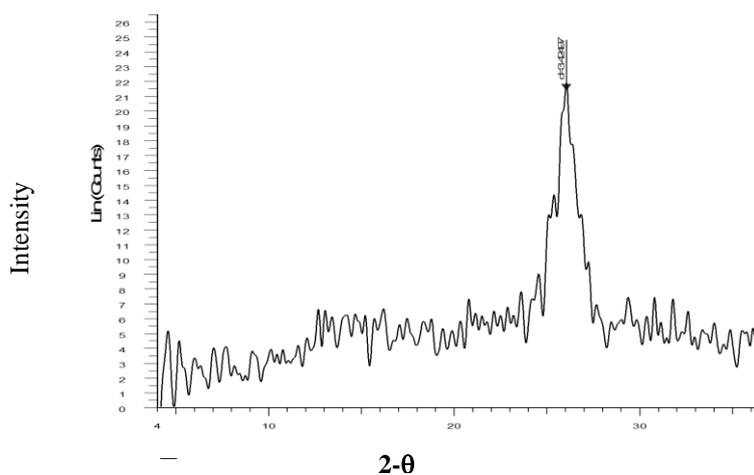


Fig. (4): X-ray diffraction (XRD) pattern of oxidized MWCNTs

Atomic ratio and percentage of the components in the MWCNTs, were estimated and it was found that the oxygen content increased after oxidizing MWCNTs by about 6.9%. Carbon content reached 90.05% and other components contents reached 3%. From Fig. 5 the TGA curve show that the MWCNTs was decomposed at 650°C at a small rate indicating highest resistance to decomposition and result residue

indicated the pure crystalline CNTs of about 87%. The obtained data show that the external and internal diameters of MWCNTs were 20-30 and 5-10 nm whereas the length was 5 μm and more and the specific surface area was $207.13 \text{ m}^2/\text{g}$. These results are in agreement with those reported by **Elsehly *et al.* (2015)**.

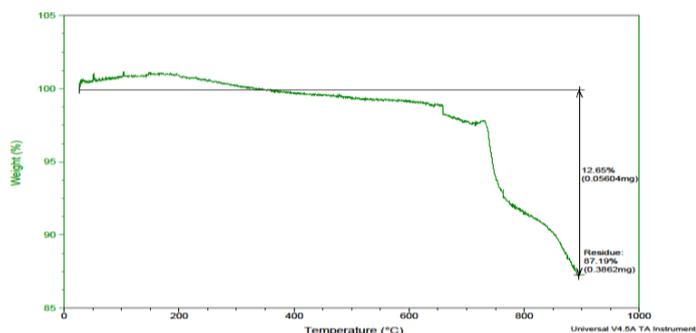


Fig. (5): TGA image of (O-MWCNTs)

Fig. (6) Shows images of SEM and TEM for ferric oxide nanoparticles which reveals the morphology of surface and a particle size average range of 5-10 nm. Fig. (7) Shows the XRD pattern for the ferric oxide nanoparticles and reveals that the main diffraction

peaks of Fe_2O_3 adsorbent at 2θ was 36.7° . EDX spectrum of ferric oxide reveals the presence of Fe, O, C and Na elements which were 44.64, 41.67, 10.97 and 2.72%, respectively. These results are in agreement with those reported by **Li *et al.* (2012)**.

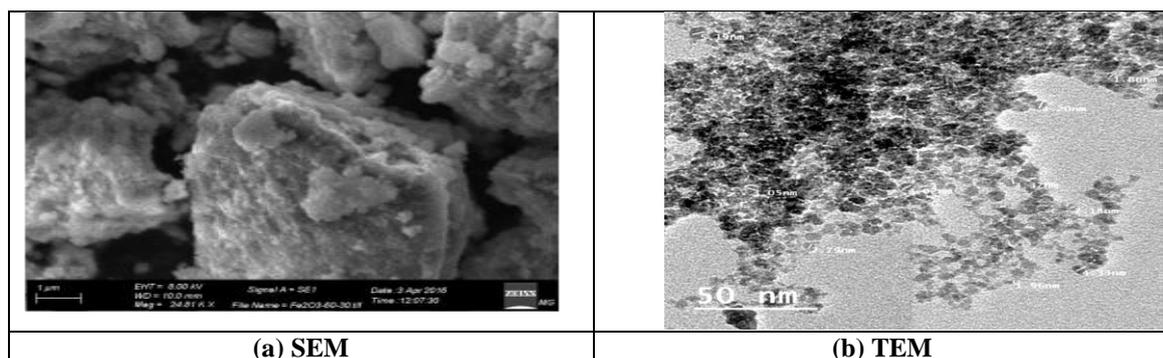


Fig. (6): SEM and TEM image of ferric oxide nanoparticles (Fe_2O_3 N.P.)

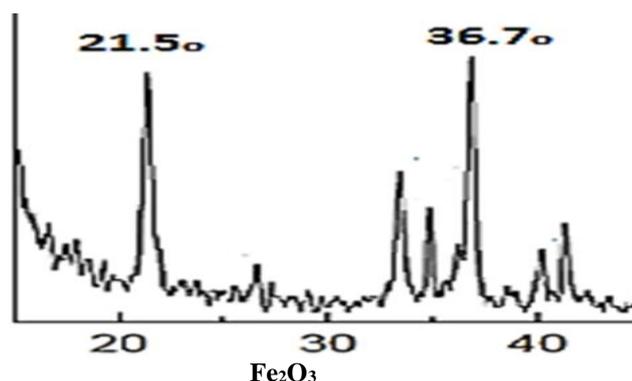


Fig. (7): X-ray diffraction pattern of the Ferric oxide nanoparticles (Fe_2O_3 N.P.)

Preliminary treatments of the ground water and industrial waste water:

This experiments, the used adsorbent mass was 0.05 g, contact time was 90 min, volume of the solute 50 mL, volume of KMnO_4 was 0.25 mL and pH 7.5 with each substance of the following adsorbents MWCNTs, Ferric oxide nanoparticles (Fe_2O_3), only and KMnO_4 with both of all these materials. Data presented in Table (2) indicate that the multi wall carbon nanotube (MWCNTs) with potassium permanganate (KMnO_4) was the best adsorbent where it resulted in the highest total removal percentage of both the metal ions i.e. Mn^{2+} and Fe^{2+} , which were the same i.e. 100%. The ferric oxide nanoparticles with

potassium permanganate (KMnO_4) was found to be the second best adsorbent. The removal percentage for Mn^{2+} and Fe^{2+} ions were found to be 91.23, 100%, respectively. On the other hand, the adsorbents multi wall carbon nanotube (MWCNTs), ferric oxide nanoparticle (NP) and potassium permanganate (KMnO_4) were found to be of low efficiency for removal of Mn^{2+} ion only which were 12.28, 31.87 and 12.28%, respectively. Despite of this materials succeeded in the removal of Fe^{2+} ion, by 97.12, 100 and 98.81%, respectively. These results are in agreements with those reported with **Ganesan *et al.* (2013)** and **Elsehly *et al.* (2015)**.

Table 2. Effects of the studied adsorbents on the investigated ground water.

Metal ion	C_0 (mg/L)	Adsorbent					
		MCNTs	NP	KMnO_4	CNTs/ KMnO_4	NP/ KMnO_4	
Mn^{2+}	3.42	Ce	3.00	2.33	3.00	0±0 ^C	0.3
		qe	±0.26 ^A	±0.01 ^B	±0.58 ^A	3.42	±0.06 ^C
		R%	12.28	31.87	12.28	100	91.23
L.S.D. for treatment 0.67							
Fe^{2+}	4.2	Ce	0.12	0±0 ^D	0.05	0±0 ^D	0±0 ^D
		qe	±0.00 ^A		±0.01 ^C	4.20	4.20
		R%	4.08	4.20	4.15	4.20	4.20
L.S.D. for treatment 0.01							

C_0 : Initial concentration of the solute.

Ce: Equilibrium concentration of the solute

qe : Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference ($P>0.05$) between any two means, within the same row have the same superscript letter.

Table (3) shows that the removal percentages of lead ion (Pb^{2+}) in waste water taken from Kaha Company of the Chemical Industries by using the Ferric oxide (NP), MWCNTs only and with potassium permanganate ($KMnO_4$). Ferric oxide nanoparticles (Fe_2O_3) as adsorbent with $KMnO_4$ was found to be more efficient than both of ferric oxide (NP) and MWCNTs without ($KMnO_4$) in reducing

concentration the heavy metal (Pb^{2+}) ion, and the removal percentages were 99.61, 91.30 and 97.61%, respectively. The multi wall carbon nanotubes (MWCNTs) with potassium permanganate ($KMnO_4$) was found to be the second best adsorbent, where it caused removal percentage of (Pb^{2+}) ion by about 99.22%.

Table 3. Effects of the studied adsorbents on the industrial waste water taken from Kaha Company of the Chemical Industries.

Metal ion	C_0 (mg/L)	Adsorbent				
		Fe_2O_3 (NP)	MWCNTs	NP/ $KMnO_4$	MWCNTs/ $KMnO_4$	
Pb^{2+}	23.00	Ce	2.00 ± 0.06^A	0.55 ± 0.02^B	0.09 ± 0.01^D	0.18 ± 0.05^C
		qe	21.00	22.45	22.91	22.82
		R%	91.30	97.61	99.61	99.22
L.S.D. for treatment 0.13						

C_0 : Initial concentration of the solute.

C_e : Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference ($P > 0.05$) between any two means, within the same row have the same superscript letter.

Treatment of some metals and heavy metal ion by using adsorbents under investigation:

Table (4) shows the adsorption behavior both of Mn^{2+} and Fe^{2+} onto MWCNTs/ $KMnO_4$, at different pH values 5.5, 6.0, 7.0, 7.5, 8.0, or 8.5 with using 0.05 g adsorbent plus 0.5 mL of MWCNTs/ $KMnO_4$ under fixed shaking time (90 min). It could be observed that

the most suitable pH value was found to be 7.5 which give the highest removal percentages of both Mn^{2+} and Fe^{2+} (100%). The charge of MWCNTs surface becomes more negative with the increase of pH, which causes electrostatic interactions. These results are in agreement with those reported by **Danka and Jan (2009)**.

Table 4. Effect of the pH on removal percentages of Mn^{2+} and Fe^{2+} ions the ground water by using MWCNTs/ $KMnO_4$.

Metal ion	C_0 (mg/L)	pH						
		5.5	6.0	7.0	7.5	8.0	8.5	
Mn^{2+}	3.42	Ce	0.50 ± 0.10^A	0.20 ± 0.06^B	0.01 ± 0.00^C	0 ± 0^C	0 ± 0^C	0 ± 0^C
		qe	2.92	3.22	3.407	3.42	3.42	3.42
		R%	85.38	94.15	99.62	100.00	100.00	100.00
L.S.D. for pH value 0.15								
Fe^{2+}	4.2	Ce	0.30 ± 0.06^A	0.20 ± 0.06^A	0.01 ± 0.01^B	0 ± 0^B	0 ± 0^B	0 ± 0^B
		qe	3.90	4.00	4.19	4.20	4.20	4.20
		R%	92.86	95.24	99.76	100.00	100.00	100.00
L.S.D. for pH value 0.10								

C_0 : Initial concentration of the solute.

C_e : Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference ($P > 0.05$) between any two means, within the same row have the same superscript letter.

Table (5) shows the adsorption behavior of lead (II) onto Fe_2O_3 / $KMnO_4$, at different pH values i.e. 4.0, 5.3, 6.0, 6.7, 7.0 and 7.5 with using 0.05 g adsorbent mass of ferric oxide plus 1 mL volume of $KMnO_4$ under fixed shaking time (120 min). The lead (II) adsorption capacity and removal percentage increased

with increasing the pH value. The metal removal percentage varied from 84.17 to 99.65% with a change in pH values from 4 to 7. These results are in agreement with those which obtained by **Intiaz and Rafique (2011)** and **Ratoi et al. (2008)**.

Table 5. Effect of the pH on the removal percentage of Pb²⁺ ion of industrial waste water with Ferric oxide nanoparticle.

Metal ion	C ₀ (mg/L)	pH						
		4.0	5.3	6.0	6.7	7.0	7.5	
Pb ²⁺	23	Ce	3.64 ±0.06 ^B	2.44 ±0.35 ^C	0.82 ±0.02 ^D	0.36 ±0.01 ^{DE}	0.08 ±0.01 ^{DE}	0.00 ±0.00 ^E
		qe	19.36	20.56	22.18	22.64	22.92	23.00
		R%	84.17	89.39	96.43	98.43	99.65	100.00

L.S.D. for pH 0.72

C₀: Initial concentration of the solute.

Ce: Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Table (6) shows the effect of KMnO₄ (0.1 M) addition on the studied metal ions (Mn²⁺ and Fe²⁺) of ground water by using 0.05 g adsorbent (MWCNTs), shaking time 90 min and fixed pH value 7.5. In this study the volumes of KMnO₄ used were in the range of 0, 0.25, 0.30, 0.35, 0.40, and 0.50 mL. The results show that the percentages of adsorbed ions Mn²⁺ and Fe²⁺ onto MWCNTs increased with increasing the volume of the applied KMnO₄. The maximum percentages of removal (R%) of Mn²⁺ ion were found

to be 12.28, 99.94, 99.98, 100, 100, 100%, respectively, while the corresponding was for Fe²⁺ removal were found to be 98.81, 99.95, 99.99, 100, 100, 100%, respectively. It could be concluded the optimum volume of KMnO₄ is 0.25 or 0.35 mL which is approximately caused the same, highest removal of both Mn²⁺ and Fe²⁺ ions, 99.94, 100% and 99.95, 100%, respectively. These results are in agreement with those reported by Odell (2010).

Table 6. Effect of volume of the added, KMnO₄ on the removal percentages of Mn²⁺ and Fe²⁺ ions of the ground water with MWCNTs adsorbent.

Metal ion	C ₀ (mg/L)	KMnO ₄ (mL)						
		0	0.25	0.30	0.35	0.40	0.50	
Mn ²⁺	3.42	Ce	3.00±0.26 ^A	0±0 ^B				
		qe	0.42	3.42	3.42	3.42	3.42	3.42
		R%	12.28	99.94	99.98	100.00	100.00	100.00

L.S.D. for KMNO₄ (0.33)

Fe ²⁺	4.2	Ce	0.05±0.01 ^A	0±0 ^B				
		qe	4.15	4.20	4.20	4.20	4.20	4.20
		R%	98.81	99.95	99.99	100.00	100.00	100.00

L.S.D. for KMNO₄ (volume) 0.01C₀: Initial concentration of the solute.

Ce: Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Table (7) shows the effect of addition of different volumes of KMnO₄ (0.1 M) i.e. 0, 0.25, 0.35, 0.5, 0.6, 0.751 and 1.25 mL on the removal percentage of the studied metal ion (Pb²⁺) from industrial waste water

by used 0.05 g ferric oxide nanoparticle with a shaking time of 90 min and fixed pH value of 7.0. The maximum percentage of removal of Pb²⁺ ion was 99.52%.

Table 7. Effect of volume of the added, KMnO₄ on the removal percentage of Pb²⁺ ion of industrial waste water with Fe₂O₃ as adsorbent.

Metal ion	C ₀ (mg/L)	KMnO ₄ (mL)								
		0.00	0.25	0.35	0.50	0.60	0.75	1.00	1.25	
Pb ²⁺	23	Ce	2.00 ±0.10 ^A	0.50 ±0.01 ^B	0.23 ±0.01 ^C	0.18 ±0.04 ^C	0.16 ±0.01 ^C	0.14 ±0.00 ^C	0.11 ±0.01 ^C	0.09 ±0.01 ^C
		qe	21.00	22.50	22.77	22.82	22.84	22.86	22.89	22.91
		R%	91.30	97.83	99.00	99.22	99.30	99.39	99.52	99.61

L.S.D. for treatment 0.12

C₀: Initial concentration of the solute.

Ce: Equilibrium concentration of the solute.

Qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Table (8) shows the relationship between the percentages of removal of Mn^{2+} and Fe^{2+} from the ground water against different weights i.e. 0.01, 0.02, 0.04, 0.05 and 0.06 g, of MWCNTs, with $KMnO_4$ under fixed pH value of 7.5, shaking time of 90 min and volume of $KMnO_4$ 0.25 mL. It could be noticed that increasing the amount of sorbent (MWCNTs) increased the percentage of removal of both Mn^{2+} and Fe^{2+} . The adsorbent weights 0.04 and 0.05 g were approximately of the same effect on the maximum percentage of removal of Mn^{2+} and Fe^{2+} (99.91, 100% and 99.81, 100%), respectively. These results are in a

good agreement with those obtained by **Pandian *et al.* (2010)**.

The removal percentage of lead (II) ion from the industrial wastewater under different adsorbent weights (0.01, 0.02, 0.04, 0.05 and 0.06 g) by Fe_2O_3 nanoparticle and the obtained results are presented in Table (8). Which revealed that the highest removal percentages of Pb^{2+} ion in the present study was 99.61% at 0.06 g ferric oxide. It was noted that ferric oxide (NP) are good adsorbent for removal Pb^{2+} ion by 99.57% at 0.05 g. These results are in agreement with those reported by **Imtiaz and Rafique (2011)**.

Table 8. Effect of the adsorbent weight (MWCNTs) and Fe_2O_3 on the removal percentages of Mn^{2+} , Fe^{2+} and Pb^{2+} ions of contaminated water.

Metal ion	C_0 (mg/L)	Adsorbent weight (g)					
		0.01	0.02	0.04	0.05	0.06	
MWCNTs							
Mn^{2+}	3.42	Ce	1.67 $\pm 0.22^A$	1.52 $\pm 0.08^A$	0.003 $\pm 0.00^C$	0 $\pm 0^C$	0 $\pm 0^C$
		qe	1.75	1.90	3.417	3.42	3.42
		R%	51.27	55.56	99.91	100	100.00
L.S.D. for adsorbent weight 0.29							
Fe^{2+}	4.2	Ce	0.20 $\pm 0.06^A$	0.14 $\pm 0.01^A$	0.01 $\pm 0.01^B$	0 $\pm 0^B$	0 $\pm 0^B$
		qe	4.00	4.06	4.19	4.20	4.20
		R%	95.24	96.67	99.81	100.00	100.00
L.S.D. for adsorbent weight 0.07							
Fe_2O_3							
Pb^{2+}	23	Ce	2.15 $\pm 0.03^A$	1.86 $\pm 0.14^B$	1.05 $\pm 0.01^C$	0.10 $\pm 0.04^D$	0.09 $\pm 0.02^D$
		qe	20.85	21.14	21.95	22.90	22.91
		R%	90.65	91.91	95.43	99.57	99.61
L.S.D. for 0.20							

C_0 : Initial concentration of the solute.

Ce: Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference ($P > 0.05$) between any two means, within the same row have the same superscript letter.

The time- profile at different periods from 15 to 90 min for adsorption of Mn^{2+} and Fe^{2+} ions onto MWCNTs at room temperature are presented in Table (9). From the obtained results, the highest adsorption capacity of Fe^{2+} occurred at 45 min of contact time and

90 min for Mn^{2+} ion. The maximum percentages of removal (R %) of these metal ions were 100, 99.81 respectively. These results are in a good agreement with those obtained by **Ganesan *et al.* (2013)**.

Table 9. Effect of the contact time on the removal percentages of Mn^{2+} and Fe^{2+} ions of ground water.

Metal ions	C_0 (mg/l)	Contact time (min)						
		15	30	45	60	75	90	
Mn^{2+}	3.42	Ce	1.06 $\pm 0.04^A$	0.54 $\pm 0.01^B$	0.29 $\pm 0.01^C$	0.12 $\pm 0.02^D$	0.01 $\pm 0.00^E$	0.007 $\pm 0.00^E$
		qe	2.36	2.88	3.13	3.30	3.41	3.413
		R%	68.91	84.21	91.52	96.49	99.71	99.81
L.S.D. for time(0.06)								
Fe^{2+}	4.2	Ce	0.40 $\pm 0.06^A$	0.01 $\pm 0.00^B$	0 $\pm 0^B$	0 $\pm 0^B$	0 $\pm 0^B$	0 $\pm 0^B$
		qe	3.80	4.19	4.20	4.20	4.20	4.20
		R%	90.48	99.98	100.00	100.00	100.00	100.00
L.S.D. for time 0.07								

C_0 : Initial concentration of the solute.

Ce: Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference ($P > 0.05$) between any two means, within the same row have the same superscript letter.

Table (10), reveals that the removal percentage of (Pb^{2+}) ion increased rapidly with increasing time. The highest capacity of Pb^{2+} adsorption occurred at 120 min of contact time where the maximum percentage of removal of Pb^{2+} was found to be 99.61%. This could

be due to the small size of ferric oxide (NP), which was favorable for the diffusion of Pb^{2+} ion onto the active sites of the solid surface. These results are in agreement with those obtained by **Zuolian *et al.* (2012)**.

Table 10. Effect of the contact time on the removal percentage of Pb^{2+} ion of industrial waste water by using ferric oxide as adsorbent.

Metal ion	C ₀ (mg/L)	Contact time (min)							
		15	30	45	60	75	90	120	
Ferric oxide									
Pb^{2+}	23	Ce	0.31 ±0.01 ^A	0.25 ±0.02 ^B	0.21 ±0.01 ^C	0.19 ±0.01 ^{CD}	0.16 ±0.01 ^{DE}	0.13 ±0.01 ^{EF}	0.09 ±0.01 ^F
		qe	22.69	22.75	22.79	22.81	22.84	22.87	22.91
		R%	98.65	98.91	99.09	99.17	99.30	99.43	99.61
L.S.D. for time 0.03									

C₀: Initial concentration of the solute.

Ce : Equilibrium concentration of the solute.

qe: Adsorbed amount at equilibrium.

R%: Removal percentage.

A, B & C: There is no significant difference ($P>0.05$) between any two means, within the same row have the same superscript letter.

Conclusion

From this study, MWCNTs which was prepared CVD with $KMnO_4$ was the best adsorbent from were efficient and economically were it resulted in highest total removal percentage of metal ions Mn^{2+} and Fe^{2+} which were 100 %. The optimum condition to removing Mn^{2+} and Fe^{2+} ion from contaminated water with MWCNTs/ $KMnO_4$, pH at 7.5, volume $KMnO_4$ 0.25 ml, sorbent mass 0.05 g, and contact time 90 min . Ferric oxide nanoparticle (Fe_2O_3) with $KMnO_4$ was found more efficient; removal percentage of Pb^{2+} ion were 99.61 %. The optimum condition to removing Pb^{2+} ion with $Fe_2O_3/KMnO_4$, pH at 6.7 volume $KMnO_4$ 1.25 ml, sorbent mass 0.06 g, and contact time 120 min.

References

- Abd-Elhakeem, M.A.; Ramadan, M.M. and Basaad, F.S. (2015)**. Removing of heavy metals from water by chitosan nanoparticles. *J. Adv. Chem*, 11: 1-7.
- Amais, R.S.; Ribeiro, J.S.; Segatelli, M.G.; Yoshida, I.V.P.; Luccas, P.O. and Tarley C.R.T. (2007)**. Assessment of nanocomposite alumina supported, on multi-wall carbon nanotubes as sorbent for on-line nickel preconcentration in water samples. *Separation and Purification Technol.*, 58: 122–128
- Atieh, M.A.; Bakather, O.Y.; Al-Tawbini, B.; Bukhari, A.A.; Abuilaiwi, F.A.; Mohamed, B. and Fettouhi, M.B. (2010)**. Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water. Hindawi Publishing Corporation *Bioinorganic Chemistry and Applications* Vol 2010, Article ID 603978, 9 pages.
- Badawy, S.S.; Shokry, S.A.; Ismail, A.A. and Zeiada, M.S. (2011)**. Study on the removal of iron (111) and chromium (III) from aqueous streams using inorganic Nanofiltration Membrane. Master of Thesis, Fac. of Science, Cairo, Univ.
- Brent, J.A. (2006)**. Review of: "Medical Toxicology". *Clin. Toxicol.*, 44: 355.
- Brunauer, S.; Emmett, P. H. and Teller, E. (1938)**. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 60: 309-319.
- Chiang, Y; Lin, W.H. and Chang, Y.C. (2011)**. The influence of treatment duration on multiwalled carbon nanotubes functionalized by H_2SO_4/HNO_3 oxidation. *Appl. Surface Sci*, 257: 2401-2410.
- Cowley, J.M. (1988)**. In high-resolution transmission electron microscopy and associated techniques; Buseck, P., Cowley, J., Eyring, L., Eds.; Oxford University Press: New York, NY.
- Danka, B. and Jan, I. (2009)**. Removal of iron and manganese from water using filtration, by, natural materials. Fac. of Civil. Engineering, Iovok, Univ. Technology, Rodlinskeho.
- Elshehly, E.M.I.; Chechenin, N.G.; Makunin A.V.; Vorobyeva E.A. and Motaweh, H.A. (2015)**. Oxidized carbon nanotubes filters for iron removal from aqueous solutions. *Int. J. New Technol. Sci. Eng.* V 2, P 14-18.
- Ganesan, P.; Kamaraj, R.; Sozhan, G. and Vasudevan, S. (2013)**. Oxidized multi walled carbon nano tubes as adsorbent for the removal of manganese from aqueous solution. *Environ. Sci. Pollut. Res.*, 20: 987-996.
- Goldstein, J.I.; Newbury, D.E.; Echlin, P.; Joy, D.C.; Lyman, C.E.; Lifshin, E.; Sawyer, L. and Michael, J. (2003)**. *Scanning Electron Microscopy and X-ray Microanalysis*; 3rd ed.; Kluwer Academic/Plenum Publishers: New York, etc.
- Gupta, V.K.; Nayak, A. and Agarwal, S. (2015)**. Bioadsorbents for remediation of heavy metals:

- current status and their future prospects. *Environ Eng. Res.*, 20: 1-18.
- Hyung, H. and Kim, J.H. (2008).** Natural organic matter (NOM) adsorption to multi walled carbon nanotubes: effect on NOM characteristics and water quality parameters. *Environ. Sci. Technol.*, Vol.42, p: 4416-4421.
- Iijima, S. (1991).** Helical microtubules of graphitic carbon. *Nature*, 354: 56-58.
- Imtiaz, A. and Rafique, U. (2011),** Synthesis of metal oxide and its application as adsorbent for the treatment of wastewater effluents. *Intern. J. of Chem. and Environ Engineering*, V 2 , Issue(6) start page, 399.
- Li, G.X.; Huaug, Y.H.; Chen, T.C.; Shih, Y.J and Zhang, H. (2012).** Reduction and immobilization of potassium permanganate on iron oxide catalyst by fluidized-bed crystallization technology. *Appli, Sci*, 2, 166-174.
- Lix, N.; Zhang, J. and Liu, Z. (2003).** Labeling the defects of single walled carbon nanotubes using titanium dioxide nanoparticles. *J. Phys. Chem., B*: 107: 2453-2461.
- Martinez, M.T.; Callejas, M.A; Benito, A.M.; Cochet, M; Seeger. T.; Anson, A.; Schreiber, J.; Gordon, C.; Marhic, C.; Chauvet, O.; Fierror, J.L.G. and Maser, W.K. (2003).** Sensitivity of single wall carbon nanotubes to oxidative processing structural modification, intercalation and functionalisation. *Carbon* 41: 2247-2256.
- Nassar, N.N. (2012).** Rapid removal and recovery of Pb^{+2} from wastewater by magnetic nanoadsorbents. *J. Hazardous Materials*, 184: 538-546.
- Odell, L.H. (2010).** Treatment technologies for ground water. Denver. American Water Works Association.
- Pandian, G.; Ramakrishnan, K.; Ganapath, S.; Subramanyan, V. (2010).** Oxidized multiwalled carbon nanotubes as adsorbent for the removal of manganese from aqueous solution. *Environ.Sci* , V 20, Issue 2, p 987 -996.
- Ratoi, M.; Bulgariu, L. and Macoveanu, M. (2008).** Removal of lead from aqueous solutions by adsorption using sphagnum moss. *Peat Politehnicavol*, 53(67): 1-2.
- Roccaro, P.; Barone, C.; Mancini, G. and Vagliasindi, F.G.A. (2007).** Removal of manganese from water supplies intended for human consumption: a case study. *Desalination*, 210: 205-214.
- Scherrer, P. (1918).** Bestimmung Der Grosse Und Der Inneren Struktur Von Kolloidteilchen Mittels Rontgenstrahlen, *Nachrichten Von Der Gesellschaft Der Wissenschaften, Göttingen, Mathematisch.Math.phys.* 2, 98-100.
- Shoushan, F.; Michael, G.C.; Nathan, R.F.; Thomas, W.T.; Alan, M.C. and Hongjie, D. (1999).** Self-oriented regular arrays of carbon nanotubes and their field emission properties. *Science*, 283: 512-514.
- Sivaram, A.; Pavel, N.; Olga, G.; Victor, G.H.; Williams, H.F.; Bradley, F. and Leonard, Y. (2004).** The characterization of single-wall carbon nanotube material. *Carbon* 42: 1783-1791.
- Steel, R.; Torrie, J. and Dickey, D. (1997):** Principles and procedures of Statistics: A Biometrical Approach, 3rd ed., McGraw-Hill, New York, NY.
- Wang, H.J.; Zhou, A.L.; Peng, F.; Yu, H. and Chen, L.F. (2007).** Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb(II) in aqueous solution. *Mater. Sci. Eng. A*, 466(1-2): 201-206.
- Zhang, H.B.; Lin, G.D.; Zhou, Z.H.; Dong, X. and Chen, T. (2002).** Removal spectra of MWCNTs and MWCNTs based H₂ adsorbing system. *Carbon*, 40: 2429-2436.
- Zuolian, C.; Annie Lai, K.; Tan Yong, T.; Dan, S.; Koh, E.T. and Xi, J.Y. (2012).** Synthesis and characterization of iron oxide nanoparticles and applications in the removal of heavy metals from industrial wastewater. *Int. J. of photoenergy*, Vol 2012, Art. ID 608298, 5 Pages.

إزالة بعض العناصر الثقيلة من المياه الملوثة باستخدام مواد الامصاص من أنابيب الكربون متعددة النانوية وأكسيد الحديد
 أسامة عبدالحميد محمد خميس* - أحمد على عبدالرحمن* - فرحات فودة على فودة* - حمدي محمد جاد**
 * قسم الكيمياء الحيوية الزراعية - كلية الزراعة - جامعة بنها
 ** مركز المعامل الحارة - هيئة الطاقة الذرية - إنشاص

تهدف هذه الدراسة الى ايجاد مواد متاحة وبتكلفة اقتصادية تصل بتركيزات المنجنيز والحديد والرصاص في المياه الملوثة المأخوذة من قها بمحافظة القليوبية الى الحدود المسموح بها باستخدام مواد ادمصاص من أنابيب الكربون النانوية وجسيمات من أكسيد الحديد في وجود برمجنات البوتاسيوم . وأيضا دراسة الخواص الفيزيوكيميائية للمواد المستخدمة والتوصل الى الظروف المثلى التي تتم عندها ازالة الأيونات موضوع البحث. في هذه الدراسة تم التوصل للنتائج التالية :- أعلى تركيزات ملوثة للمياه موضوع الدراسة كانت 3.42 و 4.2 و 23 ملليجرام/لتر لكلا من أيونات المنجنيز والحديد والرصاص بالترتيب . تمت اذالة ايونات المنجنيز والحديد باستخدام أنابيب الكربون متعددة النانوية في وجود برمجنات البوتاسيوم بينما تمت اذالة أيون الرصاص باستخدام جسيمات من أكسيد الحديد ك في وجود برمجنات البوتاسيوم . وكانت خصائص مواد المعالجة كما يلي :-

أنابيب الكربون المتعددة ذات قطر خارجي 20-30 نانوميتر وقطر داخلي 5-10 نانوميتر ومساحة السطح 13.2017 م²/جم ونسبة الكربون 90% ونسبة الأوكسجين 7% ودرجة نقاوة 87% .

جسيمات أكسيد الحديد ذات حجم حبيبات في مدى 5-10 نانوميتر ونسبة الحديد 44.64% ونسبة الأوكسجين 41.67% ونسبة الكربون 10.97% .

تم التوصل الى أن الظروف المثلى لازالة أيونات المنجنيز والحديد من المياه الملوثة عند pH 7.5 وحجم 0.25 مل من برمجنات البوتاسيوم وكمية مادة ادمصاص 0.05 جم من مادة انابيب الكربون المتعددة وزمن التلامس 90 دقيقة . بينما قدرت في حالة ايون الرصاص عند pH 6.7 وحجم 1.25 مل من برمجنات البوتاسيوم وكمية مادة ادمصاص 0.06 جرام من جسيمات أكسيد الحديد وزمن تلامس 120 دقيقة .