

# Synthesis of Magnetic Multiwalled Carbon Nano Tubes and Investigation of isotherm and kinetic models for cleanup of Carbaryl pesticide

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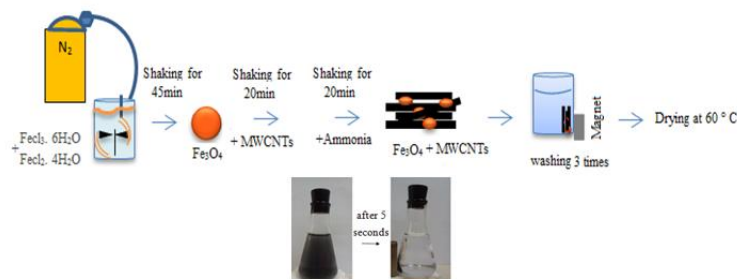
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## GRAPHICAL ABSTRACT



**Abstract:** Water is the main factor of movement and transport of pesticides and contamination of water by these pollutants is one of the most important challenges due to their widespread use and increased concentrations. Moreover, these compounds are on the U.S.EPA Priority Pollutant list because of the potential of accumulation and the property of damaging effects. In this study, multiwalled carbon nanotube-based magnetic nanoparticles were synthesized and used as an effective adsorbent for carbaryl pesticide. The properties of the synthesized  $\text{Fe}_3\text{O}_4\text{@MWCNTs}$  were characterized by TEM images and XRD analysis. The obtained data were studied by isotherm and kinetic models. Carbaryl adsorbed onto the synthesized adsorbent was compatible with the Langmuir isotherm ( $R^2 = 0.993$ ). The maximum adsorption capacity ( $q_{\text{max}}$ ) of the pesticide onto the  $\text{Fe}_3\text{O}_4\text{-MWCNTs}$  was obtained at 68.2 mg/g. The kinetic studies of the reactions showed that the adsorption process followed the pseudo-second order model with  $R^2 \geq 0.99$  for all initial carbaryl concentrations. The adsorbent was extracted by magnet reused several times (six rounds) with a reasonable efficiency. The  $\text{Fe}_3\text{O}_4\text{-MWCNTs}$  have great potential for adsorption of carbaryl from water and wastewater due to high efficiency, easy separation and reusability.

**Keywords:** Adsorption, Carbon Nanotube, Carbaryl, Kinetic, Isotherm

## 1. Introduction

Carbamates are one of the major classes of the pesticides, which are widely used in agriculture against insects, fungi and weeds (Wu et al. 2010; Liu et al. 2009). These compounds are potentially hazardous to

the environment and human health. Carbaryl (1-naphthyl-N-methyl carbamate) (scheme.1), which is a broad-spectrum insecticide, is used to control more than 100 species of insects in fruits, forests, lawns, domestic vegetables and other crops (Melchert and Rocha 2010; Zhu et al. 2009). This compound, because of their ability to accumulate and their long-term effects on living organisms, is on the priority list released by the USEPA<sup>1</sup> (Chin-Chen et al. 2012; Alavanja, Hoppin, and Kamel 2004; Liu, Zheng, and Li 2013). The potential risks of human health owing to the contact with pesticides are noticeably seen through the detection of pesticide compounds residues in water, foodstuffs and even in breast milk (El Ouardi et al. 2013). Carbaryl can cause adverse effects on humans with inhalation, skin contact, or ingestion (Chin-Chen et al. 2012). Exposure to this substance, in addition to its teratogenic characteristics, inhibits the cholinesterase enzyme, impairing the functions of the central nervous system and can cause nausea, vomit, broncho-constriction, blurred vision, convulsions, coma and respiratory failure (Chowdhury et al. 2012; Melchert and Rocha 2010; Liu, Zheng, and Li 2013).

In soil, carbaryl is bounded by organic materials and can be transported (Ghauch et al. 2001). Removal of these organic pollutants during water treatment has been tested through nanofiltration (Boussahel et al. 2000), ozonation (Kusvuran et al. 2012) and some of adsorbents such as activated carbon (El Ouardi et al. 2013; Zhang et al. 2012; Meyers, Ahlrichs, and White 2013; Chen et al. 2009). However, these techniques have some disadvantages like rapidly saturated for some adsorbents and generated byproducts. Carbon nanotubes (CNTs), due to their high surface area, have long been employed as adsorbents for trapping or separation of some contaminants from aquatic environments. But their large-scale application has somewhat been limited owing to the problems in separating materials (products and residual sorbents) from solution (Jiang et al. 2009; Wu et al. 2011). CNTs display excellent mechanical, electrical and magnetic properties (Sahoo et al. 2010).

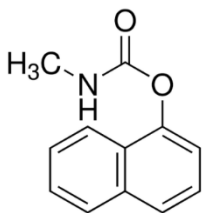
Recently, the magnetic separation method has been applied due to its low cost, economic aspects, biodegradability, non-toxicity, simplicity and being quick in separation (Kakavandi et al. 2013; Pucek et al. 2011; Mi et al. 2011; Dong et al. 2012). In this study, we synthesized and used super paramagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles in order to produce magnetic separation characteristic for MWCNTs<sup>2</sup>.

Moreover, the mechanisms of adsorption of solutions of carbaryl, as an effluent model, and magnetic MWCNTs, as the adsorbents, were chosen to be studied. Therefore, after Carbaryl sorption onto the Fe<sub>3</sub>O<sub>4</sub>-MWCNTs nanoparticles, the adsorbents could be readily separated from water solution with an external magnetic field. The basic objectives of the present work were as follows: (1) synthesizing Fe<sub>3</sub>O<sub>4</sub>-MWCNTs and presenting its properties, (2) investigating the adsorption kinetics and analyzing the experimental data with the pseudo-first-order and pseudo-second-order equations, (3) investigating the adsorption isotherms and analyzing experimental data with the Langmuir, Freundlich and BET models and (4) implementing reuse of Fe<sub>3</sub>O<sub>4</sub>-MWCNTs after adsorption.

## 2. Experimental

### 2.1 Adsorbate

Technical grade Carbaryl (C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>) of 99.9% purity supplied by Sigma-Aldrich was used as an adsorbate. The structure of the insecticide has been shown in scheme 1. Distilled water was used to prepare all solutions.



Scheme.1. Chemical structure of Carbaryl

<sup>1</sup> United States Environmental Protection Agency

<sup>2</sup> Multi Walled Carbon Nano Tubes

## 2.2 Material

Multiwalled carbon nanotubes were prepared from nano US Company, ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and ammonia were purchased from Merck (Germany).

## 2.3 Apparatus

The HPLC<sup>3</sup>, assembled from modular components (CECIL, CE4100, England), consisted of an in-line degasser, a 600E pump and a UV-visible detector (CE4200, CECIL, England). The injection loop volume was 30  $\mu\text{L}$ . A  $\text{C}_{18\text{ec}}$  column (250 mm $\times$ 4.6 mm I.D., 5.0  $\mu\text{m}$ ) MACHERY-NAGEL (German Quality) was used for separations. The mobile phase was a combination of methanol–water (70:30, v/v) at the flow rate of 1 mL/min. UV detector wavelengths were selected at 220 nm for carbaryl. The identification of carbaryl was made by retention times and ultraviolet absorption spectra detection. The peak area of the analyte was used for quantification.

The morphology of MWCNTs and  $\text{Fe}_3\text{O}_4$ -MWCNTs was characterized by transmission electron microscope (TEM) images (obtained with EM 208-Philips operated at an acceleration voltage of 100 kV). X-ray diffraction (XRD) measurement was performed using a Bruker D8Advance (CuK, radiation with 1.5416 Å wavelengths) diffractometer. In order to do magnetic separation of adsorbent from aqueous solution, we used a magnetic field with the intensity of 1.3 T; and, a pH meter (HACH-HQ-USA) was used to control solution pH ( $\pm 0.01$ ).

## 2.4 Synthesis of $\text{Fe}_3\text{O}_4$ -CNTs

Magnetic carbon Nanotubes were synthesized by a co-precipitation method.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (8.48 gr) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (2.25 gr) were dissolved in 400 ml water and mixed by mechanical stirring; then, the samples were heated at 75 °C within 45 min under nitrogen gas. Next, after homogenization in ultrasonic, 10 gr MWCNTs, were added to the solution and kept for 20 min. Afterwards, 20 ml ammonia was added to the solution. After 20 min, the  $\text{Fe}_3\text{O}_4$ -MWCNTs were separated with an external magnet and washed three times with distilled water. Finally, the nanoparticles were dried in a vacuum oven at 60 °C within 6 hours. The preparation procedure of the magnetic carbon nanotubes has been illustrated in Fig 1.

## 2.5 Adsorption kinetic and isotherm study

The parameters investigated in the current study were pH, adsorbent dose ( $\text{Fe}_3\text{O}_4$ -MWCNTs), initial carbaryl concentration and contact time. For kinetic studies, a series of 100-mL Erlenmeyer flasks were filled with 50 mL the pesticide solution at the concentration of 10 mg/L. The pH of the solution was kept at 6 by adding 0.1 M NaOH or 0.1M  $\text{HNO}_3$ . An equal amount of the adsorbent (0.2 g/L) was added separately to each flask. The agitation speed was kept constant at 150 rpm. At predetermined intervals of time (5, 10, 15, 20, 25, 30, 60 and 120 min),  $\text{Fe}_3\text{O}_4$ -MWCNTs were separated from the solution by an external magnet field.

Adsorption isotherm experiments were conducted by adding 50 mL of the solution containing 10 mg/L pesticide to different concentrations of the adsorbent (0.1, 0.15, 0.2, 0.25, 0.3 and 0.5 g/L). The mixtures were kept until 30 min at the pH value of 6.

The standard coefficient of determination ( $R^2$ ) was employed to compare the amount of fitting between prediction models and measured data.

## 3. Result and discussion

### 3.1 Characterization of magnetic carbon nanotubes

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<sup>3</sup> High-performance liquid chromatography

X-ray diffraction (XRD) measurements were employed to investigate the phase and structure of the MWCNTs and synthesized Fe<sub>3</sub>O<sub>4</sub>-MWCNTs. Diffraction peaks assigned to MWCNTs at  $2\theta = 26.5^\circ$  (Fig. 2a) can be clearly seen in the XRD curves of pure MWCNT (Wang et al. 2008), and the Fe<sub>3</sub>O<sub>4</sub>-MWCNT composite indicating the MWCNT structure was not destroyed after the successive deposition of Fe<sub>3</sub>O<sub>4</sub>. From Fig. 2b, except for the diffraction peak at  $2\theta=26.5^\circ$  resulting from MWCNTs, all the new significant diffraction peaks of the Fe<sub>3</sub>O<sub>4</sub>-MWCNT, which are matched well with the data for Fe<sub>3</sub>O<sub>4</sub>:  $30.2^\circ$ ,  $35.6^\circ$ ,  $43.3^\circ$ ,  $53.7^\circ$ ,  $57.3^\circ$ , and  $62.8^\circ$ , can be assigned to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) of the crystal indices for Fe<sub>3</sub>O<sub>4</sub>, respectively.

TEM images of MWCNTs and Fe<sub>3</sub>O<sub>4</sub>-MWCNTs have been shown in Fig 3. The outer diameters of those tubes are in the approximate range of 10–30 nm. As shown in Fig 3b, the iron oxide nanoparticles were coated on the surface of MWCNTs to form Fe<sub>3</sub>O<sub>4</sub>-MWCNTs. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were properly distributed on the surface of the carbon tubes.

### 3.2 Adsorption isotherms modeling

Three isotherms: Langmuir, Freundlich and Brunauer–Emmett–Teller (BET) were tested for their ability for description of the experimental results. The Langmuir isotherm is founded on the assumption that the adsorption process takes place on homogenous adsorbent surfaces (Kakavandi et al. 2013). This model assumes that maximum adsorption corresponds to a saturated monolayer of solute molecules on the surface of the adsorbent, with no lateral interaction among the sorbed molecules. The linear equation of the Langmuir model is shown as Eq.1:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b C_e q_{max}} \quad (1)$$

Where  $q_e$  (mg/g) is the amount of sorbed molecules per unit mass of the adsorbent,  $C_e$  (mg/L) is the adsorbate concentration at equilibrium,  $q_{max}$  (mg/g) is the maximum amount of the adsorbate per unit mass of adsorbent when complete monolayer bound at high  $C_e$  and  $b$  (L/mg) is the Langmuir constant. Fig 4 shows that the adsorption of carbaryl onto Fe<sub>3</sub>O<sub>4</sub>-MWCNTs was best fitted to the Langmuir model. The Langmuir constants ( $b$ ) and  $q_{max}$  were obtained from the intercept and slope of the plot. Characteristics of the Langmuir model can be described with the  $R_L$  factor as shown in Eq.2 (Hameed, Salman, and Ahmad 2009):

$$R_L = \frac{1}{1 + b C_0} \quad (2)$$

Where  $C_0$  is the maximum initial dose of the adsorbate (mg/L). The factor of  $R_L$  represents the condition of the isotherm to be irreversible ( $R_L=0$ ), favorable ( $0 < R_L < 1$ ), linear adsorption ( $R_L=1$ ) and unfavorable ( $R_L > 1$ ). The value of  $R_L$  in the present investigation was found to be 0.33 indicating that the adsorption of carbaryl onto Fe<sub>3</sub>O<sub>4</sub>-MWCNTs is favorable.

The BET model (Classics Brunauer, Emmett, and Teller 1938) is a development of the Langmuir model for multilayer adsorption. The BET isotherm is a theoretical equation and are commonly employed in the gas–solid equilibrium processes. It assumes that each adsorbate in the first adsorbed layer serves as an adsorption site for the second layer and so forth (Ofomaja, Unuabonah, and Oladoja 2010). In this study, this model was used to calculate Carbaryl sorption based on Eq. (3):

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{K_{BET} q_m} + \left( \frac{K_{BET} - 1}{K_{BET} q_m} \right) \left( \frac{C_e}{C_s} \right) \quad (3)$$

where  $K_{BET}$ ,  $C_s$ ,  $q_m$  and  $q$  are the constant expressive of energy of interaction with the surface, adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. A plot of  $C_e/(C_s - C_e)q$  against  $(C_e/C_s)$  should give a straight line. The values of  $K_{BET}$  and  $q_m$  can be calculated from the slope and intercept (fig.5).

The third model is the Freundlich approach; according to this model, the uptake of sorbate fall out on a heterogeneous surface by multilayer sorption (Freundlich and Hatfield 1926). The linear form of this model is presented by Eq. 4.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Where  $K_f$  (L/g) is the constant showing the relative adsorption capacity of the adsorbent and  $1/n$  is the intensity of the adsorption.  $K_f$  and  $n$  are calculated from the intercept and slope of the plot.

As can be seen from Table 1, the Freundlich model does not fit well the experimental data ( $R^2 < 0.95$ ). Thus, carbaryl adsorption onto the magnetic carbon nanotubes cannot be expressed by the Freundlich isotherm. For the Freundlich isotherm model, the value of  $n$  was greater than 1 illustrating that the adsorption process followed a normal Langmuir isotherm. This shows homogeneous magnetic carbon nanotube surface in which the carbaryl molecule and carbon nanotubes had equal adsorption activation energy (Salman and Hameed 2010).

The correlation coefficient ( $R^2$  values) was used to judge the applicability of the isotherm equation. As seen in Table 1, the Langmuir isotherm was best fitted to the experimental data while fitting the Freundlich isotherm represents a multilayer adsorption and the BET isotherm, which is an extension of the Langmuir isotherm, shows that multilayer sorption is not as good as the Langmuir model for carbaryl toxin adsorption.

The adsorption isotherm models fitted the data in the order of: Langmuir > Freundlich > BET isotherm.

### 3.3. Comparison of carbaryl adsorption capacity among different adsorbents

Table 2 compares the adsorption capacity of different types of adsorbents reported in the literature for adsorption of some pesticides. It is apparent that recycled  $Fe_3O_4$ -MWCNTs are very useful adsorbent for carbaryl removal from aqueous solutions. The value of  $q_{max}$  in this study is larger than that in most of previous works. This suggests that carbaryl could easily be adsorbed by the magnetic nanotubes.

### 3.4. Adsorption kinetic modeling

This study examined the kinetics of carbaryl removal from solutions by magnetic carbon nanotubes through the pseudo-first order and second order kinetic models as shown in Eqs. (6) and (7), respectively [28].

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where  $q_t$  (mg/g) is the adsorption at time  $t$  (min),  $q_e$  (mg/g) is the adsorption capacity at adsorption equilibrium and  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the kinetic rate constants for the pseudo-first-order and the pseudo-second-order models, respectively. The Lagergren's first-order rate constant ( $k_1$ ) and  $q_e$  determined from the model have been presented in Table 3 with the corresponding correlation coefficients. The correlation coefficients ( $R^2$ ) for the pseudo-second-order adsorption model were all higher than for the pseudo-first-order model. As can be seen from Table 3, there is no agreement between  $q_e$  experimental and  $q_e$  calculated values for the pseudo-first-order model.

The linear plots of  $t/q_t$  versus  $t$  have been shown in Fig 7 for the pseudo-second-order kinetic, yielded  $R^2$  values  $>0.99$  for all carbaryl concentrations and this showed a good agreement between the experimental and the calculated  $q_e$  values (table 3). Similar findings were claimed for carbofuran adsorption from aqueous environment through activated carbon (Salman and Hameed 2010).

### 3.5. Effect of solution pH

The effect of pH on carbaryl adsorption was investigated using 10 mg/L of initial concentration, and pH between 2 and 10 at 22 °C. The equilibrium adsorption ( $q_e$ ) was found to decline when pH increased (Fig

8). The  $q_e$  increased from 37.7 to 48.1 mg/g when pH value ranged between 2 and 10. Different physical/chemical processes like hydrolysis, complexation of ligands, redox reactions and precipitation are highly affected with pH (Mahapatra, Mishra, and Hota 2013). The pesticide adsorption onto Fe<sub>3</sub>O<sub>4</sub>-MWCNTs increased abruptly at pH ranging from 2 to 4; then, it increased slowly at pH from 4 to 10. At lower pH, the concentration of H<sup>+</sup> ion is high. Thus, it significantly influenced the protonation–deprotonation transition of MWCNT surface groups like –OH and –COOH, resulting in a competition for vacant adsorbent sites between H<sup>+</sup> ion and adsorbate molecules; for this reason, at low pH, the removal efficiency is low. Yang et al. claimed a similar pH effect on adsorption phenolic compounds adsorption trend by means of MWCNTs adsorbent (Yang et al. 2008).

### 3.6. Effect of contact time and initial concentration on carbaryl adsorption

The effects of time and initial concentration of carbaryl on the uptake using magnetic carbon nano tubes have been presented in Fig 9. The equilibrium was achieved at 30 min for carbaryl adsorption onto Fe<sub>3</sub>O<sub>4</sub>-MWCNTs. The time of equilibration adsorption was unaffected with initial concentration, but the amount adsorbed increased by increasing initial concentration of the pesticide. An increase in adsorption was observed from 24, 35.2 and 90 mg/g for initial concentrations of 5, 10 and 20 mg/L, respectively. This illustrates that initial concentration is very important in carbaryl adsorption on Fe<sub>3</sub>O<sub>4</sub>-MWCNTs. This is due to the fact that, at higher initial concentrations, carbaryl has to diffuse to the inner sites of the carbon nano tubes. Gubta et al. (Gupta et al. 2011) investigated the effect of the parameter initial concentration on adsorption of pesticides by activated carbon and they reported similar observations.

### 3.7. Reusability of Fe<sub>3</sub>O<sub>4</sub>-MWCNTs

The main objective of the reuse process is to restore the adsorption capacity of an exhausted adsorbent. The repeated availability of Fe<sub>3</sub>O<sub>4</sub>-MWCNTs for carbaryl adsorption from aqueous solution through many cycles of adsorption/desorption is quite crucial for the application of magnetic MWCNTs in the removal of pesticides from solution in real work. In this study, the reuse of Fe<sub>3</sub>O<sub>4</sub>-MWCNTs, each time after washing with distilled water, in the removal of carbaryl from aqueous solution was examined. Adsorption cycles repeated five times by using the same adsorbent for the new samples of the pesticide. Fig 10 presents adsorption percentages after reuse.

It is observed that the adsorption percentage of carbaryl declined from 94 to 77% with increasing the times of the reuse. The removal efficiency of the pesticide onto Fe<sub>3</sub>O<sub>4</sub>-MWCNTs was well after reuse for four times, which illustrates that the MWCNTs have a very good reusability.

## 4. Conclusion

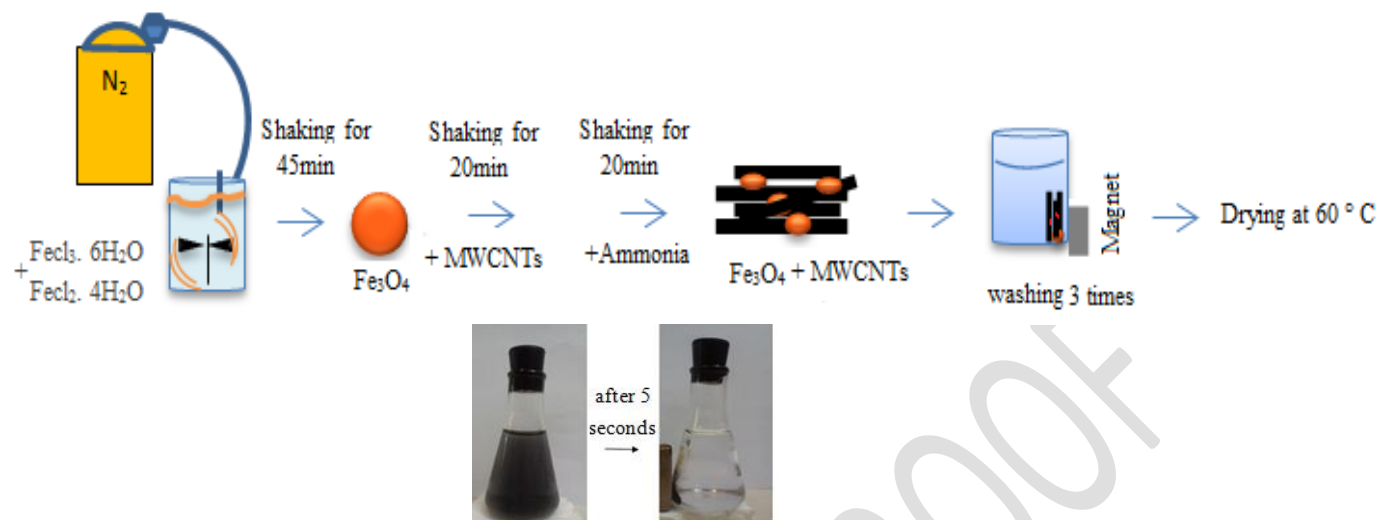
Multi-walled carbon nano tube-based magnetic nanocomposite was synthesized and it was used as an effective adsorbent for carbaryl pesticide for the first time. The XRD analysis and TEM images of the CNTs and Fe<sub>3</sub>O<sub>4</sub>-MWCNTs confirm the formation of the synthesized nanocomposite. The equilibrium data were fitted to the Langmuir, Freundlich and BET isotherm models. The suitability of the kinetic models for the adsorption of the pesticide was also discussed. It was found that the adsorption kinetics obeyed the pseudo-second-order adsorption kinetic model. After sorption, the adsorbent can be extracted and be efficiently reused for many cycles.

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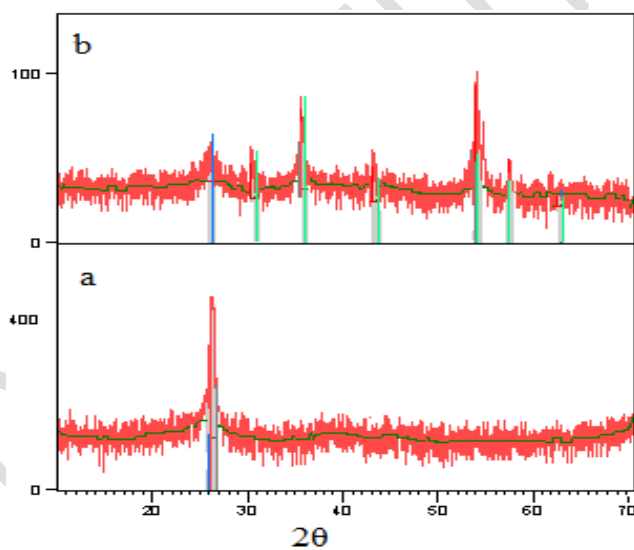
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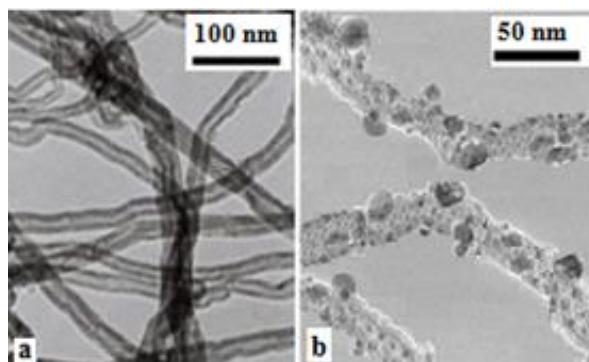
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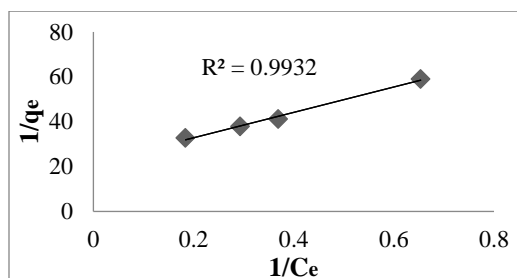
**Fig. 1.** Steps of synthesis of  $\text{Fe}_3\text{O}_4$ -MWCNTs magnetic Nano composites



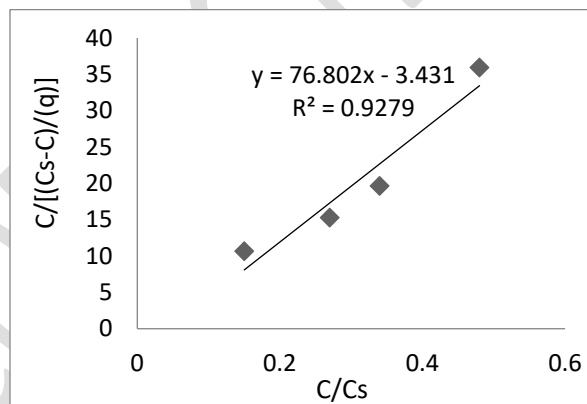
**Fig. 2.** X-ray diffraction pattern of (a) MWCNT and (b)  $\text{Fe}_3\text{O}_4$ -MWCNT



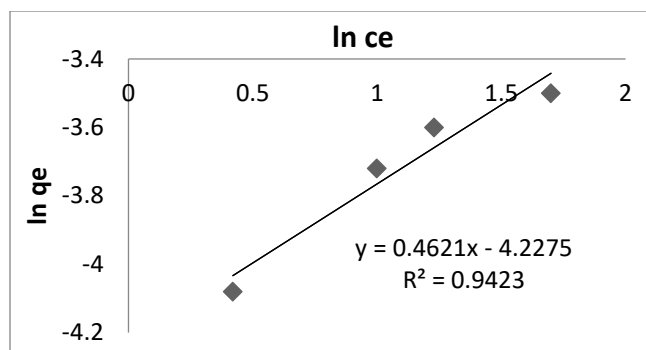
**Fig. 3.** TEM images of (a) MWCNTs and (b)  $\text{Fe}_3\text{O}_4$ -MWCNTs



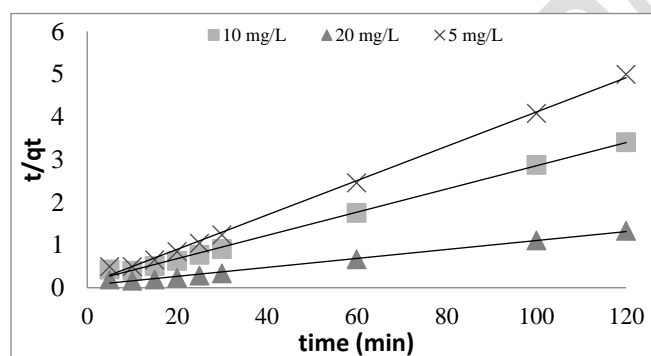
**Fig. 4.** Langmuir adsorption isotherm of Carbaryl on  $\text{Fe}_3\text{O}_4$ -CNTs



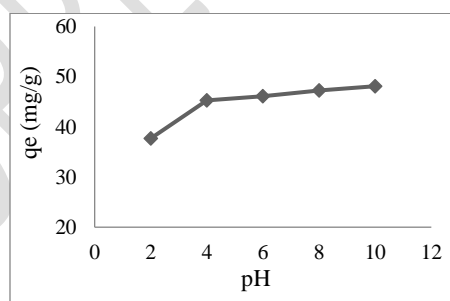
**Fig. 5.** BET adsorption isotherm of Carbaryl on  $\text{Fe}_3\text{O}_4$ -CNTs



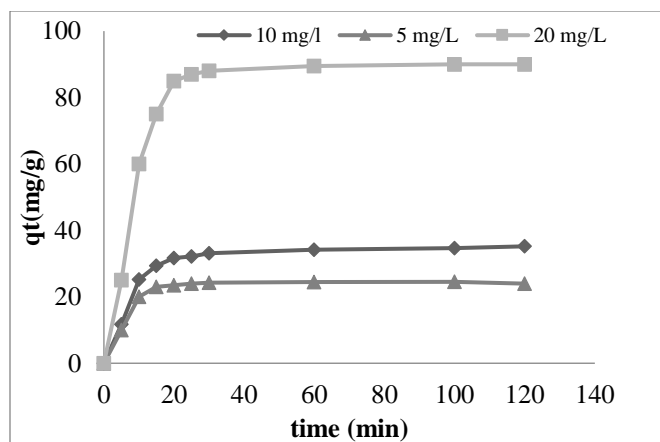
**Fig. 6.** Freundlich adsorption isotherm of Carbaryl on Fe<sub>3</sub>O<sub>4</sub>-MWCNTs



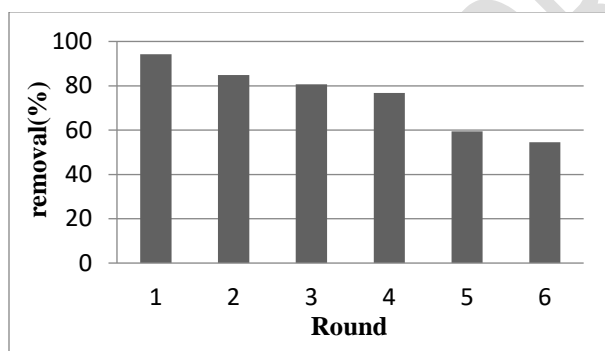
**Fig. 7.** Pseudo-second-order kinetics for adsorption of Carbaryl onto Fe<sub>3</sub>O<sub>4</sub>-MWCNTs



**Fig. 8.** Effect of solution pH on the uptake of Carbaryl



**Fig. 9.** Effect of initial concentration of Carbaryl adsorption onto  $\text{Fe}_3\text{O}_4$ - MWCNTs  
Lines represents the model fitting of pseudo-second-order equation



**Fig. 10.** Recycling use of  $\text{Fe}_3\text{O}_4$ -MWCNTs in the removal of Carbaryl from aqueous solution

**Table1.** Isotherm parameters for removal of Carbaryl by Fe<sub>3</sub>O<sub>4</sub>-CNTs

<b>Isotherm</b>	<b>Parameters</b>
<b>Langmuir</b>	
q <sub>max</sub> (mg/g)	68.2
b (L/mg)	0.212
R <sup>2</sup>	0.9932
<b>Freundlich</b>	
K <sub>f</sub>	12.64
n	1.51
R <sup>2</sup>	0.9423
<b>BET</b>	
K <sub>BET</sub>	20.847
q <sub>m</sub>	18.783
R <sup>2</sup>	0.9279

**Table 2.** Comparison of adsorption capacity of different pesticides mentioned in this work and previous studies

<b>Pesticide</b>	<b>Adsorbent</b>	<b>Qmax</b>	<b>R2</b>	<b>reference</b>
carbaryl	Fe <sub>3</sub> O <sub>4</sub> -MWCNTs	68.2	0.993	The current study
carbaryl	Clay	10.75	0.97	(Mahmoud El et al. 2013)
Methyl parathion	Activated carbon	97.09	0.998	(Gupta et al. 2011)
Atrazine	Activated carbon	95.24	0.995	(Gupta et al. 2011)
Methoxychlor	Activated carbon	66.67	0.995	(Gupta et al. 2011)
Deltamethrin	oil shale ash	10.74	0.997	(Al-Qodah, Shawaqfeh and Lafi 2007)
Paraquat dichloride	Pyrolysis and activation of used tires	27.8	0.991	(Hamadi, Swaminathan and Chen 2004)
8-quinolinecarboxylic acid	Sodium montmorillonite	65.4	0.98	(Mekhloufi et al. 2013)
8-quinolinecarboxylic acid	Organic-acidic montmorillonite	75.9	0.99	(Mekhloufi et al. 2013)
Carbaforan	banana stalks activated carbon	161.3	0.989	(Salman and Hameed 2010)
Aldrin	acid-treated date stones	6.37	0.913	(El Bakouri et al. 2009)
Dieldrin	acid-treated date stones	6.97	0.901	(El Bakouri et al. 2009)
Endrin	acid-treated date stones	5.98	0.924	(El Bakouri et al. 2009)

**Table 3.** Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental  $q_e$  values attained at different initial carbaryl contents

Initial concentration(mg/ L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			pseudo-second-order model		
		$k_1$	$q_{e,cal}$ (mg/g)	$R^2$	$k_2$	$q_{e,cal}$ (mg/g)	$R^2$
5	24.5	0.084	7.5	0.8162	0.0131	25.52	0.9972
10	35.2	0.035	10.59	0.8173	0.0054	36.78	0.9968
20	90	0.086	49.21	0.8764	0.0017	97.57	0.9922