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Synthesize and Application of the Fe_3O_4/MW-CNT Composite in the Photo-Catalyst Assisted Electrochemical Oxidation of BTX Compounds From Wastewater

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ABSTRACT

The Fe_3O_4/MW-CNT composite was prepared for a hybrid photo-catalyst-assisted electrochemical process for the removal of BTX contaminants from wastewater. The oxidation of multi-walled carbon nanotube was conducted by different treatments including the acid treatment and hydrogen peroxide. The XRD, FTIR, SEM, TEM, and BET analyses were performed to characterize both the MW-CNT and the synthesized composite. Simultaneous photo-catalyst and electrochemical processes were conducted to evaluate the performance of a new hybrid process for wastewater treatment. The effect of the current density, photo-catalyst loading, and BTX initial concentration was investigated experimentally. The characterization results of the synthesized composite show that a mixture of strong nitric acid and sulfuric acid treatment at a high exposure time and low temperature is the best route for the oxidation of MW-CNT. The removal efficiency of BTX compounds from wastewater using the hybrid photo-electrochemical process was found to be in the range of 28 to 43% under different conditions. The optimum condition for the maximum removal of BTX was found by the mathematical modeling of experimental data. The results indicate that a combination of photo-catalyst and the electrochemical process can enhance the BTX removal efficiency.

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1. Introduction

Health concerns with regard to organic and inorganic pollutants in the environment, caused the regulation of higher standards for water contaminating pollutants by different authorities around the world [1]. These regulations increased the need for more advanced treatment technologies. the photo-catalyst oxidation process is a promising technology for the oxidation of different kinds of environmental pollutants, specifically for wastewater treatment [2]. Carbon nanotubes (CNTs) are increasingly used in many research fields such as electronics, mechanics, sensor application [3-6] as well as environmental applications [7]. For instance, Mubiayi et al. used MWCNT for enhancing clay properties [4]. Ravindran et al. used MWCNT to reinforce the formaldehyde nanocomposite to improve the electrical properties of the composite [6]. Employing CNTs for such applications requires the modification of its surface by introducing functional groups such as hydroxyl group (OH), carbonyl groups (C=O), and carboxylic group (COOH) [3, 8]. These functional groups can improve the dispersibility of nanotubes in aqueous solutions. Functionalizing a nanotube for a specific application requires a proper method [9]. The most common liquid materials that are utilized for the chemical oxidation of CNTs are HNO_3, H_2SO_4, H_2O_2, and $KMnO_4$ [10]. It has been found that the acid treatment is more effective in introducing carbonyl and carboxylic functional groups compared to the peroxide treatment [11, 12]. Many studies have been conducted on the oxidation of CNTs by the acid treatment [13].

Since the acid treatment may damage the nanotubes by fragmentation (shortening), it must be conducted with care. The effect of the treatment time (reaction time), acid strength, treatment temperature, and type of CNTs have been investigated in previous studies [3, 8, 10, 11, 14-18]. It was shown that the higher reaction time increased the oxygenated functional groups on the surface of CNTs, but it also fragmented the nanotubes [15]. Hiura et al. [19] used a mixture of nitric and sulfuric acids at different ratios for the oxidation of CNTs. It was observed that the higher acid strength caused the nanotube fragmentation [19]. In a similar study using a mixture of nitric acid and sulfuric acid, it was found that the damage to nanotubes could be controlled by changing the exposure time [16]. From literatures, it can be concluded that the optimal condition for the successful treatment of nanotubes is essential. Although, different methods yield different characteristics for the nanotubes. Functionalized nanotubes can be used for various applications such as photo-catalysts, adsorption, and synthesizing new composites. In the last few decades, wastewater treatment by the oxidation process with magnetic nanoparticles (MNP) has been the subject of many research studies [18, 20]. Magnetic nanoparticles with CNTs composites are used for photocatalytic applications [14, 18]. In particular, the Fe_3O_4/MWCNT composite has been prepared and utilized for the adsorption of benzene, toluene, and xylenes (BTX) compounds [17] and 2,4,6-trinitrophenol (TNP) from the aqueous phase [21]. The synthesis of magnetic nanoparticles coated on MWCNT requires proper MWCNT oxidation with no fragmentation to nanotubes and a simple synthesis route.

The destruction and removal of BTX compounds from wastewater, when the concentration of these compounds is higher than 20 mg/L, are not efficient with photocatalytic and other advanced oxidation processes [22]. On the other hand, the electrochemical process for the removal of an

organic compound can take lots of energy and time for the effective removal of these materials [23]. When the concentration of these contaminants is high, a combination of the oxidation processes in series is required. To the best of our knowledge, the idea of using these processes simultaneously in one step is not investigated in literatures. The idea is to reduce the time and energy requirement of the electrochemical process by a photo-catalyst and enhance the removal process of these organic contaminations at the same time. It seems a viable option in large-scale processes where time and energy are vital factors.

In this study it is aimed to synthesize a magnetic photocatalyst for the oxidation of organic compounds in wastewater with the combination of electrochemical processes. Therefore, in the first step, a multi-walled carbon nanotube was functionalized using various chemical treatments. Then, the functionalized multi walls CNTs were used for the synthesis of the Fe_3O_4/MWCNT composite. Afterward, the synthesized composite was applied in a hybrid photo-catalyst / electrochemical oxidation process. The effect of various factors in this hybrid process was investigated by an experimental design procedure. Finally, the optimal condition for this hybrid process was determined.

2. Experimental Procedure

2.1. Preparation of the functionalized MW-CNT

Pure MWCNTs (‘‘MW-CNT’s 150 F’’) with the outer diameters of less than 20 nm, an inner diameter of about 3 nm, and a typical length larger than 0.6 mm were purchased from the US NANO. Nitric acid, sulfuric acid, hydrogen peroxide, and a combination of these materials are used for the chemical activation. The type and concentration of reagents used for oxidation experiments are presented in Table 1.

Table 1
Experimental condition of the MWCNT oxidation.

Label	Reagent 1	Reagent 2	Reflux temp (C)	Reflux time (h)	Additional treatment
a	20ml HNO_3 68%	60ml H_2SO_4 98%	80	4	-
b	40ml HNO_3 3M	40ml H_2O_2 35 v%	80	4	Double reflux
c	30ml HNO_3 68%		80	2	
d	20ml HNO_3 68%	60 ml H_2SO_4 98%	47	17	Mixing and reflux

In each treatment, 0.3g of MWCNTs was added to a flask containing agent 1 and agent 2 as mentioned in Table 1 (except for sample B). Then the flask is sonicated for 1h in a conventional ultrasonic bath at 30 ℃ to reduce damages to the MWCNT. Afterward, the solution was refluxed at 80 °C and then centrifuged, filtered, and washed successively with distilled water. The black material was dried in an oven at 150 ℃ for about 10h. In experiment C, the MWCNT/HNO_3 solution was sonicated for 1h and then refluxed at 80 ℃ for a period of 4h. Next, the solution was centrifuged and washed several times with distilled water. Then, the black material was mixed with a 35 v% H_2O_2 and refluxed at 55 ℃ for 2h. The solution was filtered and the filtrate was washed with distilled water. Finally, the filtrate was dried in an oven at 150℃ and stored in a sealed bottle for the next steps.

2.2. Characterization of the functionalized MWCNT

Fourier Transform Infra-Red (FT-IR) spectra were obtained on KBr discs containing a very small amount of the MWCNTs to identify the functional groups. The FT-IR analysis was conducted with a Nicolet-Protege 460 in the spectral range of 600 to 4000 cm^{-1}. Also, FE-SEM and EDX analyses were carried out in a JEOL, JSM-6360-LV equipment using a voltage of 20–25 kV to recognize the functionalized MWCNTs.

2.3. Synthesis of the Fe_3O_4/MWCNT composite

Typically for the synthesis of the Fe_3O_4/MWCNT composite, 0.1 g of the functionalized MWCNT was dispersed in 100 mL of deionized (DI) water with the aid of ultra-sonication. Then, $FeCl_3$ (1.08g, 0.004 M), and Ammonia (2.16 g, 0.036 M) were added to the MWCNT solution. The mixture was refluxed at 100°C for 24h under stirring. The obtained black solid was washed with DI water and dried overnight at 105°C. The dried material was calcined at 350°C for 4h with the nitrogen flow.

2.4. Characterization of the composite

Infrared spectra of the composite sample were obtained by a Fourier Transform Infra-Red spectrophotometer (FT-IR, Varian 2000). Also, X-ray diffraction (XRD) spectra were used to examine the phase purity of the prepared samples. The XRD spectrum was obtained with the aid of a powder X-ray diffractometer (‘X’ pert MPD diffractometer) using the CuKα radiation. The morphology of the sample was examined using a field emission scanning electron microscope (FE-SEM, Hitachi S-3500N) coupled with an energy-dispersive X-ray spectroscope (EDS), and a transmission electron microscope (TEM, JEOL-3010, Japan) equipped with EDS operated at an accelerating voltage of 300 kV.

2.5. Hybrid photo-catalyst / electrochemical process

These experiments are aimed to investigate the combination of photochemical and electrochemical processes for the removal of BTX compounds. To perform these experiments, an experimental apparatus was used. This experimental apparatus consists of an electrochemical cell and a light source for photochemical reactions. The electrochemical cell consists of two 3*15 cm electrodes (graphite as cathode and iron as anode electrodes with a 3cm distance between them). The cell was connected to a DC source with voltage and current regulators. The reactor consists of a 1L glass vessel.

In each test, a predetermined weight of wastewater with a known concentration of BTX was added to the reactor vessel. Then a known weight of the synthesized composite was added to the reactor and mixed for a few seconds and then the electrodes were placed at a 3cm distance from each other and the test started by applying current with a DC regulator. The setup was stopped after 30min and the photo-catalyst was collected by a magnet. Then the solution was centrifuged and filtered by a nano-filter to remove the residual photo-catalyst. The chemical oxygen demand of the filtered solution was measured by the COD tester. The removal efficiency of the process was calculated by the following relation:

$$\eta = \frac{COD_F - COD_I}{COD_I} \times 100 \qquad (1)$$

Where η is the removal efficiency, COD_F and COD_I are the final and initial CODs of the solution, respectively.

The main parameters that affect the removal performance of BTX including the current density, initial concentration of BTX in the wastewater, and photo-catalyst loading in the process, were considered. Therefore, an experimental design using the central composite design (CCD) with three parameters at 3 levels was performed. The parameters and the levels are presented in Table 2. The time of the reaction was kept constant at 60 min for all experiments.

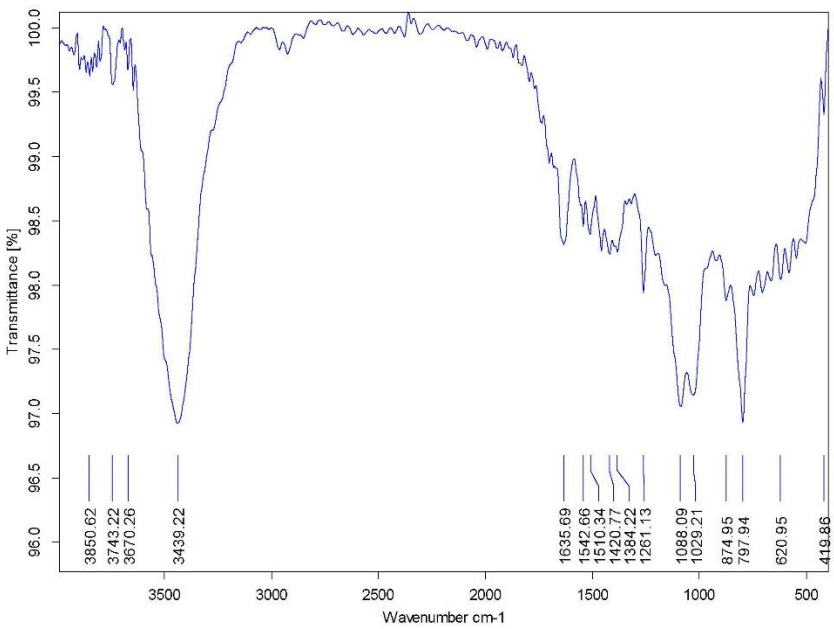
Table 2
Experimental parameters for the photo-electrochemical process.

Parameter	Unit	Level -1	Center	Level +1
Initial concentration of BTX	(g/L)	1	3	5
Photo-catalyst loading	(g/L)	0.1	0.2	0.3
Current density	(Ahm)	20	60	100

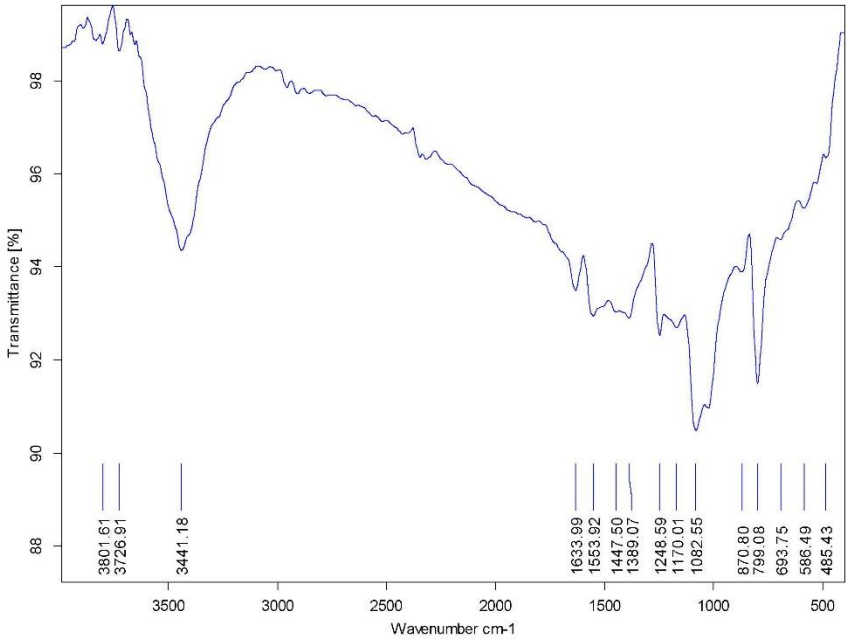
3. Results and Discussions

3.1. Infrared spectroscopy

The results of the FT-IR spectroscopy of the oxidized samples are presented in Figure 1. The stretching at the range of 3430-3440 cm^{-1} band is attributed to the hydroxyl group (OH) of the MWCNT. Peaks at the 2920 cm^{-1} range indicate asymmetric and symmetric CH_2 bond stretching. The stretching of the C=C bond is indicated by peaks at 1630 cm^{-1} spectra. The sample treated with nitric acid and sulfuric acid at a high reflux time and low temperature shows the presence of hydroxyl and carbonyl functional groups (peak at 1714 cm^{-1} in Figure 1d).



(a)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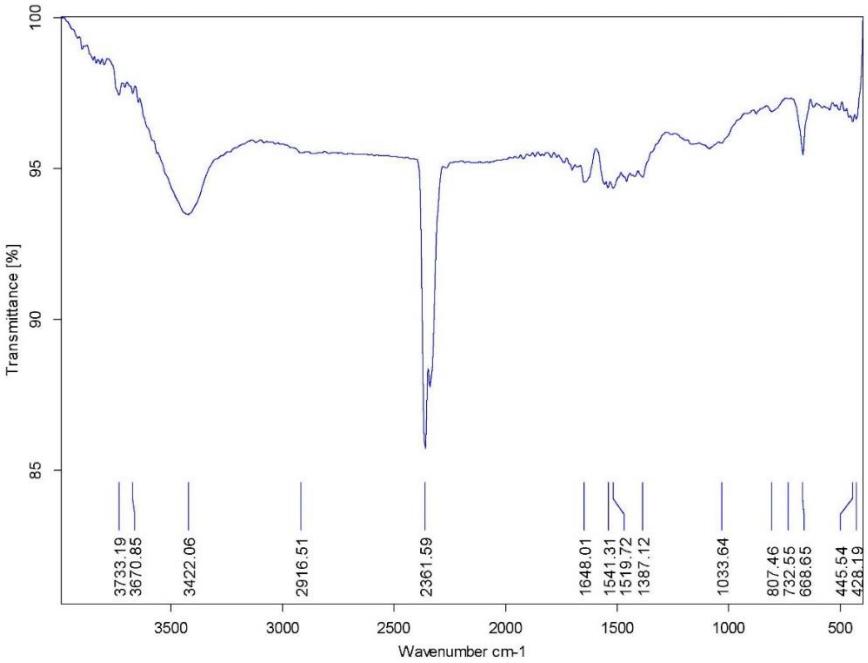
799.08
693.75
586.49
485.43

(b)


Transmittance [%]
Wavenumber cm-1
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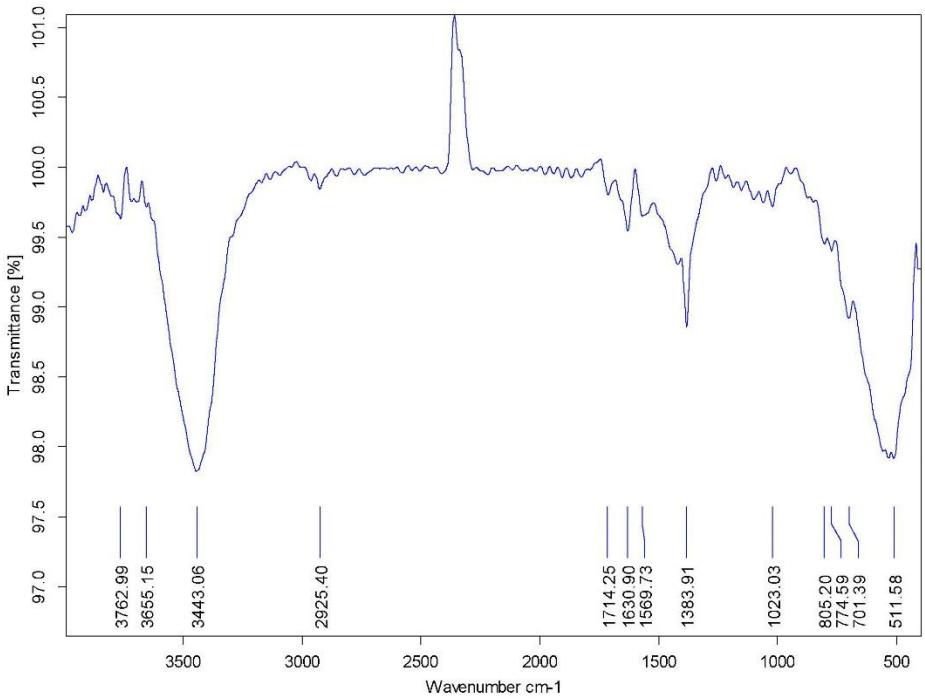
807.46
732.55
668.65
445.54
428.19

(c)



(d)

Figure 1. FT-IR spectra of treated MWCNTs. a) sample treated with nitric acid and sulfuric acid (ratio 1:3 v/v) and the reflux temperature of 80 °C b) sample treated with nitric acid and H_2O_2, c) sample treated with nitric acid d) sample treated with nitric acid and sulfuric acid (ratio 1:3 v/v) and the reflux temperature of 47 °C.

The higher acid strength along with lower oxidation time was not able to produce desired functional groups on the surface of the MWCNT. By increasing the time of oxidation even at lower temperatures, an oxygenated functional group was produced on the surface of MWCNT. Another noteworthy observation was that a mixture of nitric acid and hydrogen peroxide was not able to produce carbonyl functional groups on the surface, instead it generates C-O bounding on the surface (peak at 1042 cm^{-1}) (Figure 1b). Based on the FTIR patterns for treated samples, it can be concluded that the treatment with a mixture of nitric acid and sulfuric acid (ratio 1:3 v/v) at low temperatures and higher reflux times is more effective (Figure 1d). The double treatment with nitric acid and hydrogen peroxide in series also can produce different functional groups which are required for the synthesis of MWCNT composites.

The FT-IR spectroscopy result for the Fe_3O_4/MWCNT composite is presented in Figure 2. The sample d of the treated MWCNTs was used to synthesize the composite. In Figure 1d, it can be seen that the presence of Fe_3O_4 nanoparticles in he composite structure occupies carbonyl functional groups and also C-O bonds. The hydroxyl groups are related to band 3419 cm^{-1} which shows a slight shift from 3443 cm^{-1} for the treated MWCNT with nitric acid and sulfuric acid. The strong peaks at 622, 1174, and 1623 cm^{-1} are attributed to Fe-O, C-O, and C=O, respectively.

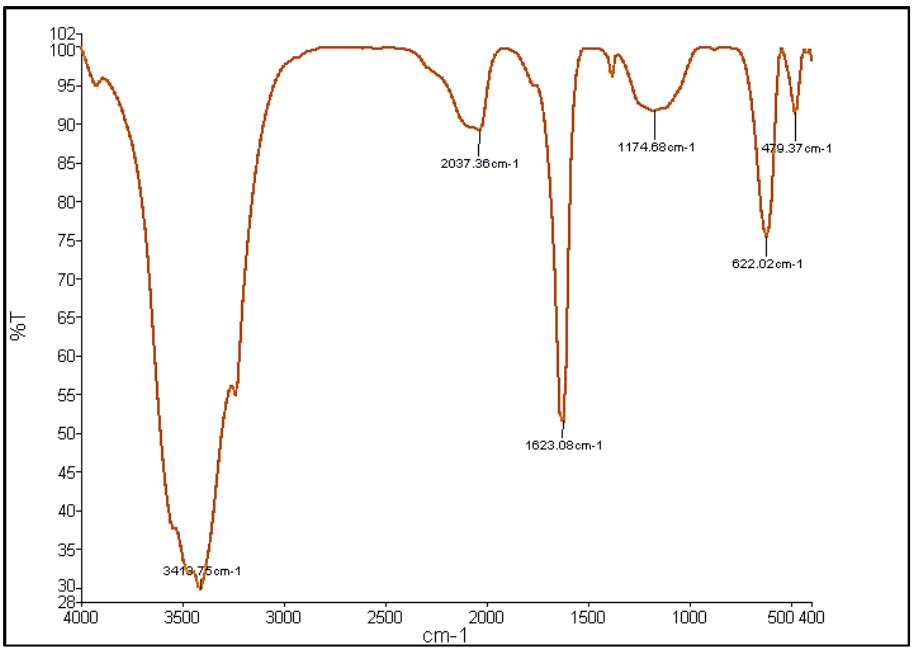
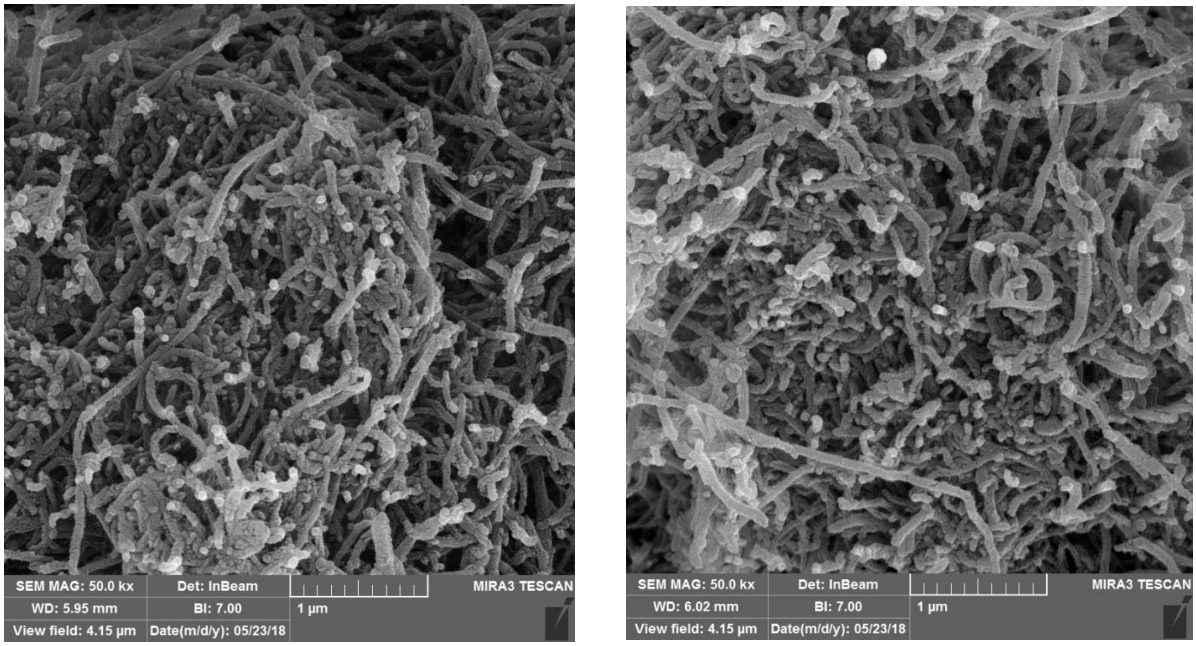


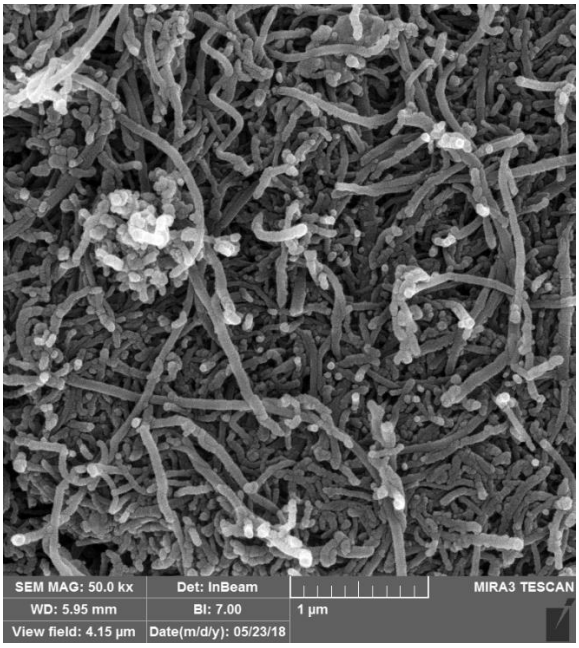
Figure 2. FT-IR spectrum of the synthesized Fe3O4/MWCNT composite.

3.2. FE-SEM and EDX analysis

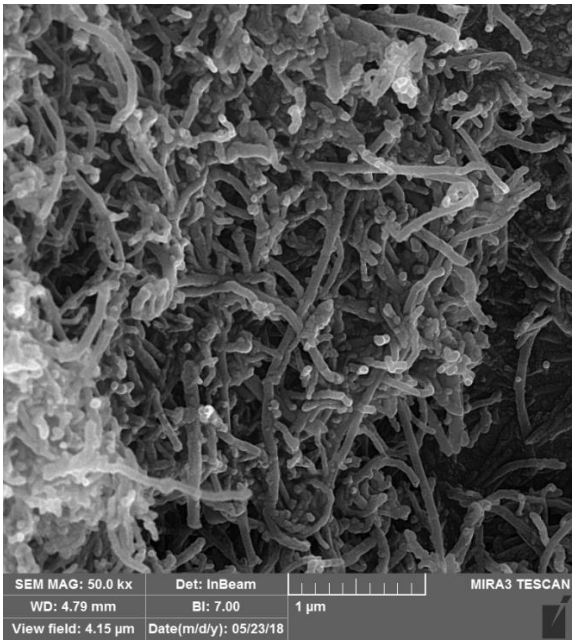
The results of the scanning electron microscopy of all treated samples are presented in Figure 3. This analysis was conducted to investigate the fragmentation of MWCNTs due to the acid treatment. The SEM images show a similar morphology for all treated samples. A qualitative analysis of the tube's length reveals a range of 1-3 µm for the tubes which is similar to the as-received original MWCNTs. The measurement of the tube's diameter in all samples indicated that the tube's diameter for all samples was in the range of 40-60 nm which is similar to the as-received material.



(a) (b)



(c)



(d)

Figure 3. Scanning electron microscopy of treated MWCNTs. a) sample treated with nitric acid and sulfuric acid (ratio 1:3 v/v) and the reflux temperature of 80 °C b) sample treated with nitric acid and H_2O_2, c) sample treated with nitric acid d) sample treated with nitric acid and sulfuric acid (ratio 1:3 v/v) and the reflux temperature of 47 °C.

No damage to the tubes can be seen at 50kx magnification (Figure 3). The energy-dispersive X-ray analyses of the treated samples are presented in Table 3. The EDX analysis shows no impurities in MWCNT samples due to the nature of the acids that are used in this study.

Table 3
EDX analysis of treated MWCNT samples.

Elements	**Treated samples**			
	a	b	c	d
C (A %)	93	80	70	78
O (A %)	6.64	20	30	15
S (A %)	0.36	-	-	7
Non detected	-	-	-	-

As it can be seen, the largest part of MWCNT consists of carbon. The acid treatment by nitric acid and sulfuric acid introduced sulfur into the MWCNT structure. The higher acid treatment time helps to increase the amount of sulfur in the structure (sample d). Treatment with nitric acid and hydrogen peroxide introduces more oxygen to the tube structures. Treatment with nitric acid alone introduced the highest amount of oxygen into the structure (sample c). Also, the lower temperature treatment of nitric acid and sulfuric acid introduced more sulfur to the structure of MWCNT (sample d).

3.3. XRD pattern of the composite

The XRD pattern of the synthesized composite versus the treated MWCNT is shown in Figure 4.

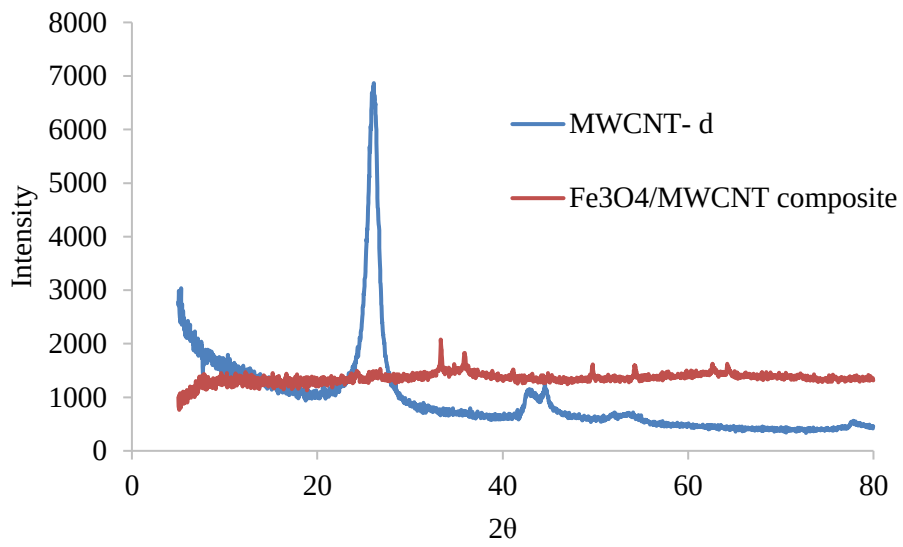


Figure 4. X-ray diffraction pattern of the treated MWCNT and Fe_3O_4/MWCNT composite.

The results show that the presence of Fe_3O_4 particles in the composite changes the XRD pattern. The Fe_3O_4/MWCNT XRD pattern obtained in this study is in agreement with that presented in literatures [11].

3.4. TEM of the composite

The Transition Electron Microscopy (TEM) of the synthesized composite has been conducted to evaluate the presence of Fe_3O_4 particles in the sample. The TEM image is presented in Figure 5.

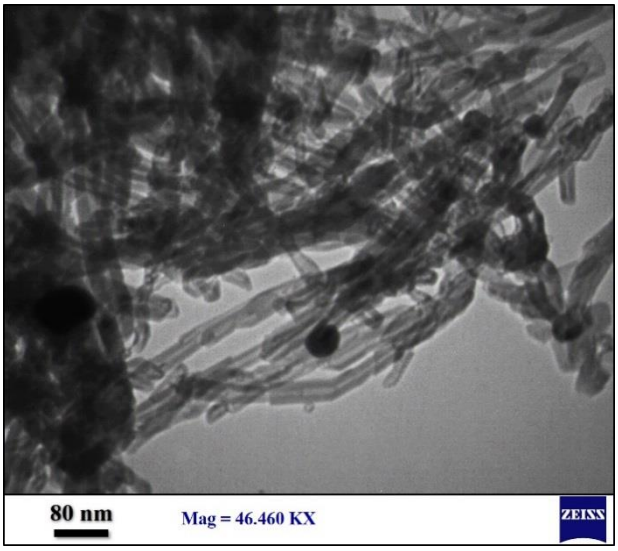


Figure 5. TEM image of the Fe_3O_4/MWCNT composite.

The image shows that the outer surface of the MWCNT is grafted by the Fe_3O_4 particle. Also, the average particle size of 40nm was measured by the TEM observation.

3.5. BET analysis of the composite

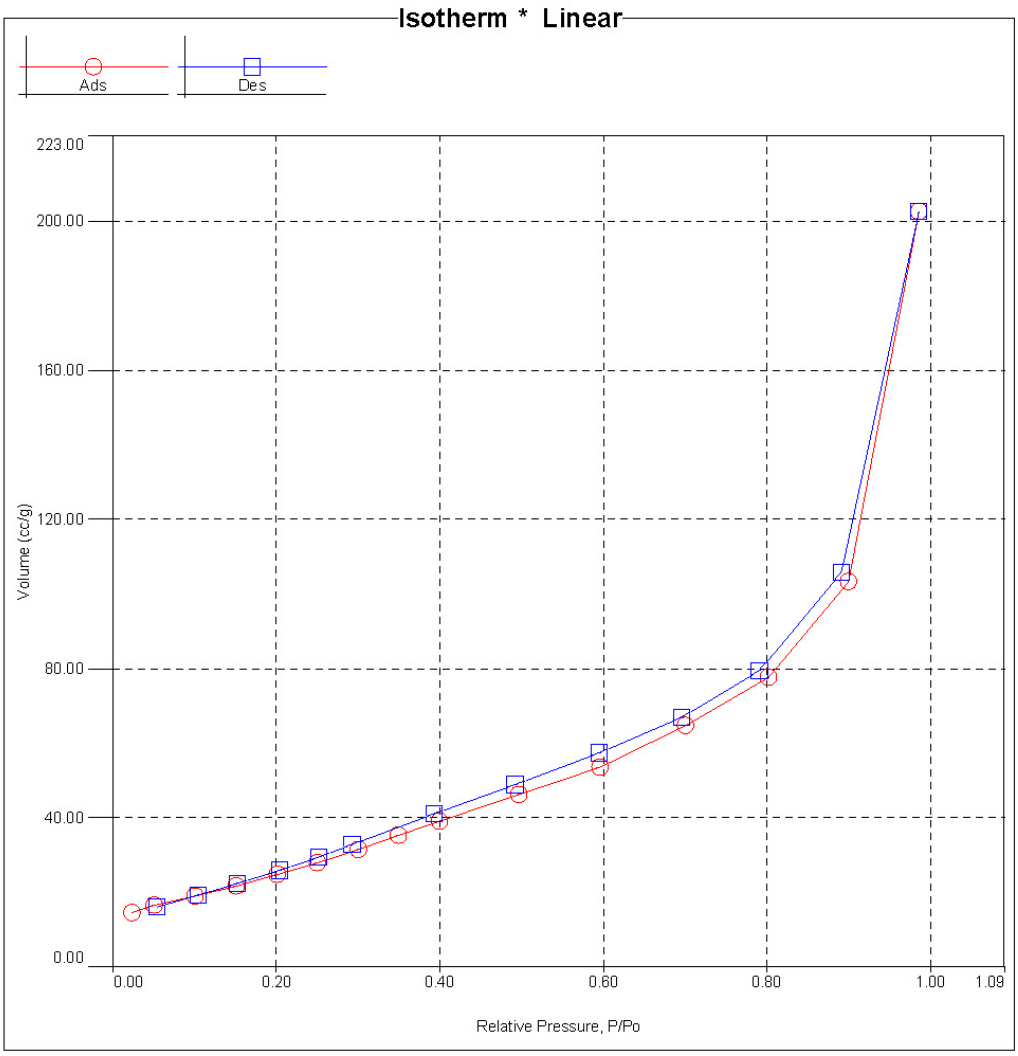
The measurement of the BET surface area of the MWCNT before and after adding Fe_3O_4 nanoparticles is presented in Table 4. As it can be seen, by introducing the Fe_3O_4

nanoparticles into the surface of the MWCNT, the surface area has been increased but the pore volume has been decreased. It is plausible that introducing nanoparticles into the MWCNT structure may block some of the MWCNT pores, therefore the pore volume decreases.

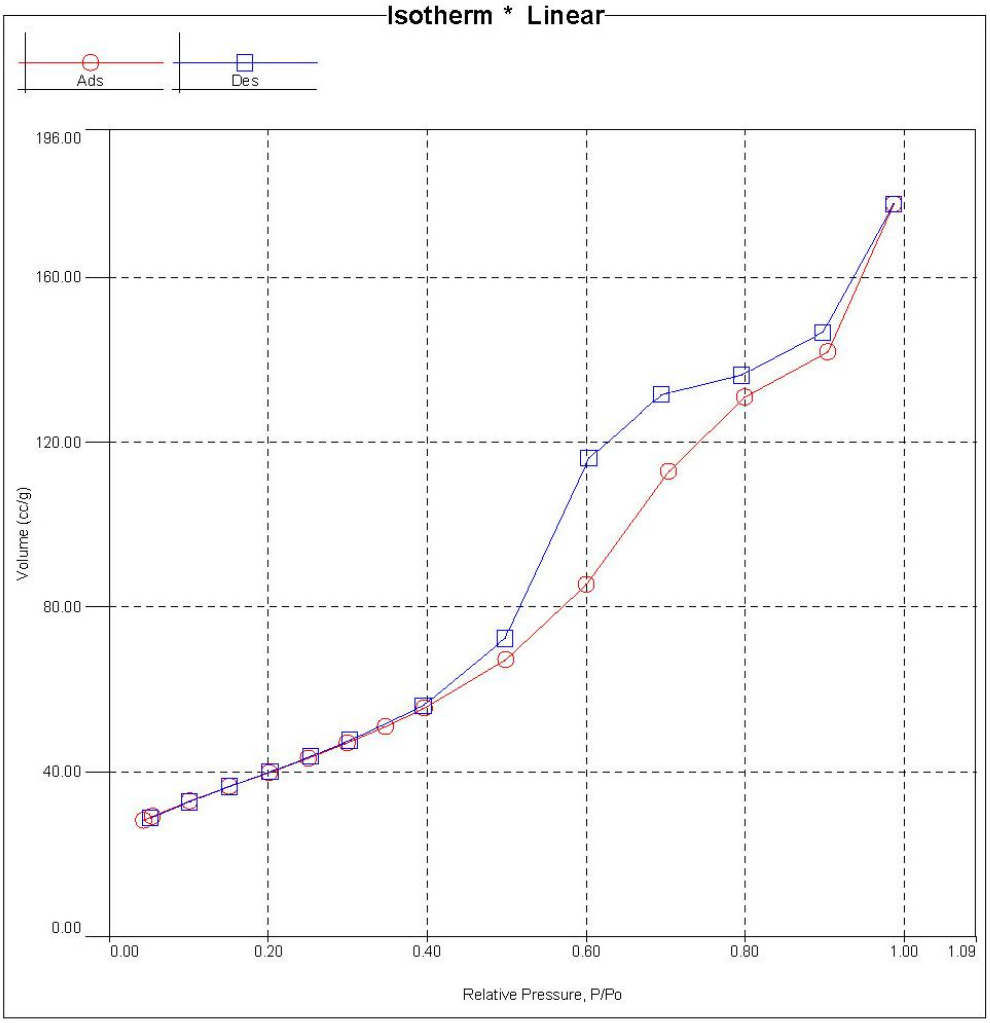
Table 4
Measurement of the BET surface area of the MWCNT and Fe_3O_4/MWCNT composite.

Sample	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore diameter (nm)
MWCNT	135	0.329	2.73
Fe_3O_4/MWCNT composite	176.6	0.284	4.62

N_2 adsorption-desorption isotherms at 77 K are presented in Figure 6. Introducing the Fe_3O_4 particles on the surface of nanotubes changes the adsorption behavior of MWCNT. The adsorption isotherm changes and hysteresis occurs at a relative pressure of about 0.4 which indicates the mesoporous structure of the composite. The adsorption isotherm in type IV (IUPAC classification) also confirms that the pore is a well-defined cylindrical-shaped pore or agglomerates with a uniform spherical shape [14].



(a)



(b)

Figure 6. N_2 adsorption/desorption of MWCNT and the Fe_3O_4/MWCNT composite, (a) Treated MWCNT, and (b) Fe_3O_4/MWCNT composite.

3.6. Removal of BTX from wastewater

The experimental results of the COD reduction with a hybrid photo-catalytic-electrochemical oxidation process are presented in Table 5. As it can be seen, the maximum removal efficiency was observed for the concentration of 1 g/L of BTX and the catalyst loading of 0.3g/L and a current density of 100 Ahm with the corresponding COD removal of 43%. In comparison, Zhang et al., [23] achieved a conversion of 25% for the benzene removal with the electrochemical oxidation with 3V of voltage and a reaction time of 30 min with Pt/rGO/CFP electrodes. Bina et al. [1] reported a value of more than 97% of the BTX removal for MWCNT and nano Fe with an initial concentration of 10 mg/L of BTX compounds and a reaction time of 10 min. However, in this study, it was used a 100 times higher value of the BTX concentration which may have resulted in the lower BTX removal. Also, in this study it was measured the COD removal instead of the BTX concentration changes due to oxidation.

Table 5
Experimental design table and the corresponding COD% removal

Run	A-concentration	B- loading	C- Current density	COD removal %
1	5	0.2	60	32
2	5	0.1	20	28
3	3	0.3	60	35
4	1	0.3	20	32
5	3	0.2	60	33
6	3	0.2	100	42
7	1	0.2	60	35
8	3	0.2	60	35
9	1	0.1	20	27
10	3	0.2	20	28
11	5	0.3	20	30
12	1	0.3	100	43
13	5	0.3	100	40
14	5	0.1	100	37
15	3	0.1	60	35
16	1	0.1	100	42

The design matrix evaluation for the response surface quadratic model shows that no alias was found for the quadratic model fit test. Therefore, this model was used to fit the experimental data. The ANOVA results for the quadratic model are presented in Table 6.

Table 6
ANOVA results of the quadratic model fit to experimental design data.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	374.6	3	124.8667	64.7257	< 0.0001	significant
A-concentration	14.4	1	14.4	7.464363	0.0182	
B- loading	12.1	1	12.1	6.272138	0.0277	
C- Current density	348.1	1	348.1	180.4406	< 0.0001	
Residual	23.15	12	1.929167			
Lack of Fit	21.15	11	1.922727	0.961364	0.6703	not significant
Pure Error	2	1	2			
Cor Total	397.75	15				

The Model's F-value of 64.73 implies the model is significant. There is only a 0.01% chance that a "Model's F-Value" could occur due to noises. Values of "Prob > F" less than 0.0500 indicate that the model terms are significant. In this case, A, B, and C are significant model terms. The "lack of fit F-value" of 0.96 implies the lack of fit is not

significant relativly to the pure error. There is a 67.03% chance that this large "lack of fit F-value" could occur due to noises. It seems that the current density is the most effective factor in the removal process. The model parameters are reported in Table 7.

Table 7
Model regression results

Std. Dev.	1.389	R-Squared	0.942
Mean	34.625	Adj R-Squared	0.927
C.V. %	4.011	Pred R-Squared	0.887
PRESS	44.887	Adeq Precision	23.615

The "Pred R-Squared" of 0.887 is in reasonable agreement with the "Adj R-Squared" of 0.927 and the "Adeq Precision" measures the signal-to-noise ratio of which the value greater than 4 is desirable. In this study, the ratio of 23.615 indicates an adequate signal. Based on these results, the final equation of the model in terms of the actual factors is as follows:

COD Removal % =+25.375 - 0.600* Concentration + 11.000* Loading + 0.1475* Current density (2)

The optimization of the model has been performed with the design expert v7.0 software. The target of the optimization was set to maximize the COD% removal and other parameters in the range. The final optimum condition is presented in Table 8:

Table 8
Optimum condition for the experimental removal of BTX by the hybrid photo catalyst-electrochemical oxidation process.

Concentration	Loading	Current density	COD %	Desirability
1	0.3	100	42.83	0.989

The results show, the optimum condition for the maximum removal of BTX by the hybrid photo-catalyst/electrochemical process has been achieved by the concentration of 1g/L of BTX, catalyst loading of 0.3 g/L, and current density of 100 Ahm. The corresponding maximum value of COD% removal was estimated to be 42.83% and the desirability of this value was 0.989 which is near the ideal value of 1.

4. Conclusion

In this study, the oxidation of multi-wall carbon nanotubes was conducted by different treatments, and the Fe_3O_4/MWCNT composite was synthesized by the chemical decomposition and hydrothermal treatment. The experimental results indicate that the treatment with acid nitric and sulfuric acid at a lower temperature with a higher reaction time is the most effective route for the oxidation of MWCNT without fragmentation or destruction to the nanotubes. Although the use of the two-step reflux by acid nitric and hydrogen peroxide in series introduced the high-oxygenated functional group to the surface, it was unable to introduce the carbonyl groups to the MWCNT. The Fe_3O_4 particles were well dispersed and grafted to the surface of the MWCNT. The BET surface area of the Fe_3O_4/ MWCNT composite increased compared to that of MWCNT while the pore volume of the composite decreased in contrast to that of MWNCT. The hybrid photo-catalyst/electrochemical process was successfully employed for the BTX removal from wastewater. The experimental design was employed to measure the effect of different parameters on the removal efficiency. The optimum condition for the BTX removal by this hybrid new technique is higher than that of conventional methods. Comparing the

results of this study with related literatures, it can be concluded that this hybrid process is promising for the removal of organic compounds from wastewater. This process consumes less energy and reduces the processing time but the economics of the process should be considered for large-scale industrial wastewater treatments.

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