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SYNTHESIS OF CARBON NANOTUBES FROM GRAPHITE AND INVESTIGATION OF THE CATALYTIC ACTIVITY OF MWCNTs/Cr₂O₃-NiO WITH THE REMOVAL OF BISMARCK BROWN G DYE FROM ITS AQUEOUS SOLUTION

UDC 539

This work describes the synthesis of carbon nanotubes from graphite by the chemical precipitation method and nanocomposites of multiwall carbon nanotubes (MWCNTs) with co-oxide nanocomposite (MWCNTs)/MO(Cr₂O₃-NiO). Those nanocomposites were prepared with the use of a simple evaporation and a drying process. The obtained composites were characterized, by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. The activity of the prepared composites was investigated by the following removal of a Bismarck brown G dye (BBG) from the aqueous solution via photocatalytic reactions. The efficiency of the photocatalytic dye removal over the prepared composites was 91.43% after one hour of reaction under the optimal conditions, which were a mass dosage of 0.03 g, pH = 5, and a temperature of 30 °C.

Keywords: dyes removal, Bismarck brown G, carbon nanotubes, nanocomposite.

1. Introduction

Nanotechnology deals with matter at dimensions of 1 to 100 nm and studies the synthesis, characterization, and applications of materials on a nanoscale. Nanomaterials are materials in a nanostructure, have at least one dimension on the nanoscale (1–100 nm), and possess different chemical and physical properties that are better than those of bulk materials, because of their size and structure [1]. The chemical and physical properties of nanomaterials can differ from those of bulk materials of the same composition such as their melting temperature, color, charge capacity, and magnetic properties [2]. The general fields of nanotechnology include nano electronics, nano chemistry, nano biology, nano medicine, and nano pharmaceuticals. Nanoscale materials have very important applications to an environment to prevent the pollution and remove pollutants; the most important applications of nanotechnology are in the treatment of wastewaters [3, 4]. Carbon is one of the most important elements on the Earth and

has different images like amorphous carbon, graphite, graphine, diamond, activated carbon, fulleren, and carbon nanotubes [5]. In 1991, multiwall carbon nanotubes (MWCNTs) were discovered as a secondary product of the fulleren preparation [6]. The simplest carbon nanotube is composed of a single sheet of a honeycomb network of carbon atoms called graphene, and it is rolled up seamlessly into a tubular form. The walls of these tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. Carbon nanotubes (CNTs) are characterized as cylinders of carbon atoms in three dimensions and have hybridization sp² which is stronger than the hybridization sp³ of diamond. Carbon nanotubes are the example of nanotechnology with sizes less than 100 nm [7, 8]. CNTs are insoluble in all solvents due to strong van der Waals interactions that tightly hold them, but the chemical functionalization of CNTs enhances the solubility in various solvents and produces novel hybrid materials potentially suitable for applications. CNTs have a very wide range of applications such as catalysts, sensors, transistors, membranes, electrodes, elements of solar and fuel cells, etc.) [9].

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Combined with metal oxides (MOs), CNTs can produce new composites with new interesting properties. In addition, combining these materials on the nanoscale can reduce some of their disadvantageous properties. As a result, the nanocomposites have large applications in comparison with the separated nanoparticles, because CNTs act as a carrier to stabilize the nanoparticles. CNT/MOs nanocomposites have high specific surface areas with active surfaces for the physical and chemical adsorption. In this context, different parameters such as the initial concentration of an organic pollutant, contact time, adsorbent dosage, pH of a reaction mixture, and effect of the presence of other cations and anions in the reaction mixture need to be optimized [10, 11].

The present study describes the preparation of MWCNTs from graphite and nanocomposites. Then the activity of these prepared composite materials (MWCNTs/Cr₂O₃-NiO) is investigated with the removal of Bismarck brown G dye (BBG) by photocatalytic reactions in those prepared nanocomposites.

2. Experimental Part

2.1. Materials and instruments

Sulfuric acid, hydrochloric acid HCl, and nitric acid were obtained from BDH, and hydrogen peroxide H₂O₂, potassium permanganate KMnO₄, and Bismarck brown G with the molecular formula (C₂₁H₂₄N₈2HCl) were obtained from Al-Hilla Textile Factory-IRAQ.

Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), and Raman spectroscopy were used to determine the chemical bonds present in samples.

2.2. Chemical precipitation method

This method is based on the oxidation of graphite or graphene with concentrated sulfuric acid and KMnO₄. This mixture was dissolved in a required amount of DW with stirring at 5 °C. Then this mixture was mixed with H₂O₂ 30%. The obtained precipitate of graphite oxide was separated and washed with HCl (10%). It was treated with HNO₃ 70% and distilled water and sonicated at room temperature for six hours. Then this precipitate was washed with excess amount of DW to remove any residual remaining acid [12].

2.3. Synthesis of the nanocomposite

Nanocomposite of (MWCNTs/ Cr₂O₃-NiO) was prepared, by using a simple evaporation and drying process. This composite was prepared by adding MWCNTs to MO (MO = Cr₂O₃-NiO) in the mass ratio 1:0.5 g. Then MWCNTs were dispersed into 100 mL, and MO was added into 20 mL of distilled water. The mixtures of MWCNTs and MO were stirred, respectively, for 35 min and 20 min. Then mixture of MWCNTs was added into the MO suspension with the stirring and heating to 80 °C to evaporate water from the obtained mixture. After that, the obtained composite was dried for overnight in an oven at 100 °C [13].

2.4. Photocatalytic activity of the prepared nanocomposite

In this study, the photocatalytic process was performed with the use of a Philips-Holland mercury lamp (250 W) without cover glass as a source of UV radiation, magnetic stirrer, hot plate, and photoreaction cell 30 mL in volume, which was made from Pyrex glass with quartz windows. The experiment was performed by introduction of the nanocomposite material and the aqueous solution of BBG 50 ppm, 30 mL, into the photoreaction cell. The temperature of the reaction mixture was adjusted at 30 °C, pH = 5, and nanocomposite dosage of 0.03 g for one hour [14].

Before the irradiation, the suspensions were stirred in darkness for 10 min with a magnetic stirrer to ensure the adsorption equilibrium. Then we draw 1–2 ml every 10 minutes from the reaction mixture, collected, and centrifuged for 20 min. The supernatant liquid was carefully removed, by using a syringe with a long elastic needle, and then centrifuged again at the same speed and for the same time. The second centrifugation was found necessary to remove fine particles of the catalyst. After the second centrifugation, the absorbance at a maximum wavelength of 468 nm of the BBG was measured with a UV-visible spectrophotometer (UV-1650PC Shimadzu, Japan).

2.5. Nanocomposite characterization

2.5.1. X-ray Diffraction (XRD)

The crystal structure of the prepared nanocomposite was investigated, by using the powder X-ray anal-

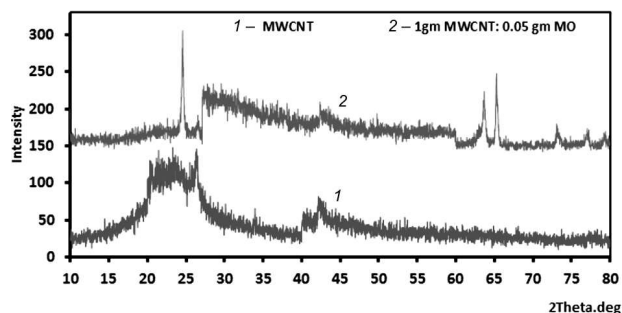


Fig. 1. XRD patterns of CNT and composite for CNTs prepared by the chemical precipitation method

ysis, Philips X-ray diffraction with $\text{CuK}\alpha$ radiation (1.542 \AA , 40 KV, 30 MA), in the 2θ range, 10–80 degrees. XRD6000, Shimadzu, Japan.

2.5.2. Fourier Transform Infrared spectroscopy (FTIR)

Functional groups on the surface of the prepared composite were investigated using FTIR, 8400S Shimadzu Japan. FTIR spectra were recorded in the range $400\text{--}4000 \text{ cm}^{-1}$, materials were mixed with a powder of KBr in a ratio of 1.2.

2.5.3. Raman spectroscopy

Raman spectroscopy is used to characterize the conductance properties or the diameter of the tubes as a powerful method for determining the degree

Table 1. Diffraction angles 2θ , d -relative intensity for F-MWCNTs and nanocomposite prepared from graphite

Sample	2θ (deg.)	d (\AA)	I/I_0
CNT	24.43	3.793	100
	25.91	7.388	100
	34.01	6.582	50
	42.46	2.126	60
	43.80	2.335	80
Nano composite MCNTs : co-oxide 1 mg : 0.05 g	26.73	3.331	100
	37.83	2.735	40
	39.81	2.262	4
	42.76	2.112	60
	62.96	1.475	80
	65.10	1.667	90
	77.95	1.567	30
	79.87	1.730	40

of structural ordering or the presence of contaminants [15]. This technique was used to distinguish between the types of CNTs. There are five important features to distinguish CNTs by (RBMs) radial breathing modes. For SWCNT, there is a very intense band at 105 cm^{-1} , while MWCNTs have a very weak band. The disordered mod D band referred to amorphous carbon or defect style of CNT (sp^3) appears at 1339 cm^{-1} , whereas the tangential mod G band (crystalline carbon sp^2) related to the vibrations in sp^2 is revealed at 1580 cm^{-1} . The increased intensity of the G band as compared to the D band is likely referred to the lower number of graphene layers, which means the borderlines between single-walled, few-walled, and multiwalled cases. MWCNT D band and G band are almost similar, but the intensity of G band for SWCNT is stronger and more intense than D band. The second-order harmonic G' is referred to the charge exchange between the tube and the guest moiety. It appears very clearly at 2672 cm^{-1} . The band at 2930 cm^{-1} is considered as the $\text{G} + \text{D}$ band, its very weak band for MWCNT did not appear clearly. The ratio of the D to G band intensities (I_D/I_G) is an important parameter to distinguish between the types of carbon, it characterizes the disordered site of a CNT wall. If the ratio I_D/I_G is low, this means SWCNTs, while the high ratio means MWCNTs [16].

3. Results and Discussion

3.1. XRD of prepared CNTs and nanocomposite from graphite by the chemical precipitation method

The XRD patterns in Fig. 1 and Table 1 show the presence of new peaks at 25.91° and 42.46° for CNTs. XRD patterns in Fig. 1 of the MWCNTs/co-oxide composite are very similar to that of neat co-oxide that prepared by the co-precipitation method.

3.2. FTIR spectroscopy of MWCNTs

Fourier transform infrared spectral data of MWCNTs are presented in Fig. 2. FTIR spectra of MWCNTs show a peak around 1633 cm^{-1} , which is assigned to $\text{C}=\text{C}$ of alkenes, and that around $1500\text{--}1400 \text{ cm}^{-1}$ is assigned to the $\text{C}\text{--}\text{C}$ stretching in the aromatic ring. The FTIR spectra of F-MWCNTs show a peak around 1741 cm^{-1} assigned to $\text{C}=\text{O}$ stretching vibrations of a carboxyl group. The peak

around 3394 cm^{-1} is assigned to the OH vibration mode of O-MWCNTs [17].

3.2.1. FTIR spectroscopy of MWCNTs/ Cr_2O_3 -NiO nanocomposite

The FTIR spectra of the MWCNTs/MO nanocomposites are shown in Fig. 3. From these spectra, three obvious peaks, which correspond to metal-oxygen bonds, OH bonds, and H bonds, are observed. These arise possibly due to the intermolecular interaction at the surface of MO. However, the three absorption peaks of the MWCNTs/MO nanocomposite are shifted toward higher wavelengths due to stronger interactions between the polar groups on the MO and functional groups at the surface of MWCNTs [18].

3.3. Raman spectra of MWCNTs and MWCNTs/MO nanocomposite prepared by the chemical method

Figure 4 shows the Raman spectrum of MWCNTs prepared from graphite and its composite at a ratio 1 gm MWCNT:0.5 gm MO. The disordered mode (D mode) of MWCNTs appearing at 1345 cm^{-1} corresponds to the sp^3 hybridized carbon atoms, and the tangential mode (G mode) is revealed at 1576.0 cm^{-1} . The D and G bands for the prepared CNTs have similar intensities, which means that the prepared carbon nanotubes are multitype [19]. Another bands appear at 2680.0 cm^{-1} (G^-) as the first overtone of D. The ratio of intensities I_D/I_G decreases from 1.2748 to 0.8. The bands of MWCNT/MO are shifted due to the strong interaction between the MO and MWCNTs. D band appears at 1350.0 cm^{-1} , G 1597.0 cm^{-1} , $\bar{\text{G}}$ 2697 cm^{-1} , and G + D 2010 cm^{-1} .

Table 2. A_t/A_0 of BBG dye for MWCNT/ Cr_2O_3 -NiO

Time (min)	A_t/A_0
0	1.0000
10	0.3910
20	0.1049
30	0.1030
40	0.0972
50	0.0957
60	0.0895

3.4. Photocatalytic removal of BBG dye over nanocomposite

The results of the photocatalytic BBG dye removal over nanocomposite with a mass of 0.03 g, $\text{pH} = 5$, and at $30\text{ }^\circ\text{C}$ are shown in Fig. 5 and Table 2. The aqueous solution (50 ppm) of the dye 30 mL in

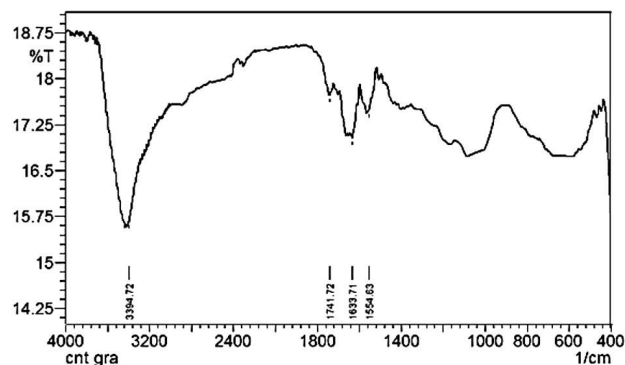


Fig. 2. FTIR spectra of F-MWCNTs prepared from graphite

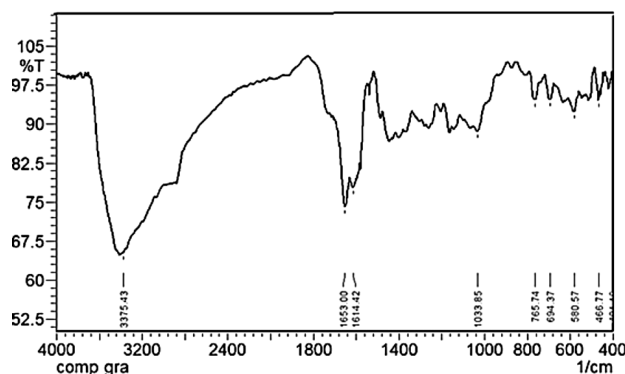


Fig. 3. FTIR spectra of the F-MWCNTs (gra)/ Cr_2O_3 -NiO nanocomposite

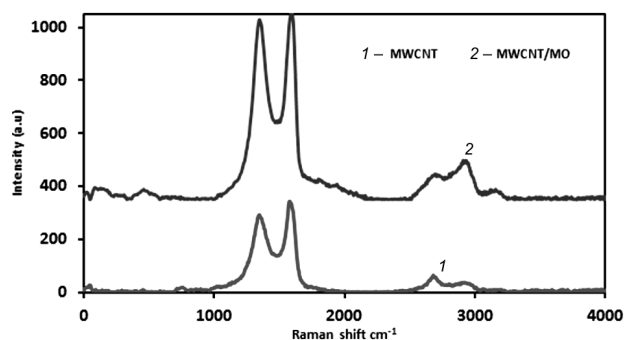


Fig. 4. Raman spectra of F-MWCNTs and FMWCNTs/MO prepared by the chemical method

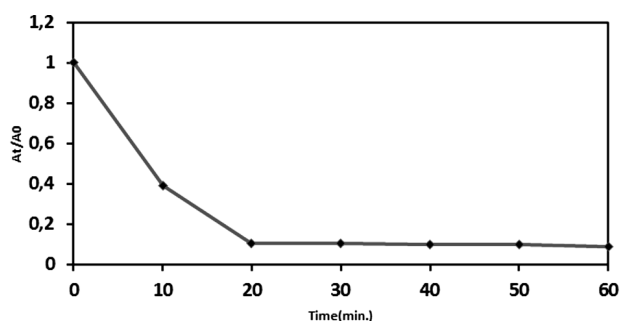


Fig. 5. Removal efficiency for BBG dye

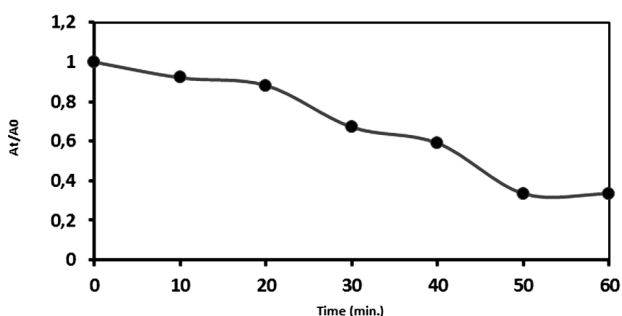


Fig. 6. Remaining percentage of the adsorption of BBG dye

Table 3. Remaining percentage of the adsorption of BBG dye for MWCNT/Cr₂O₃-NiO

Time (min)	A_t/A_0
0	1.000
10	0.921
20	0.882
30	0.671
40	0.590
50	0.335
60	0.335

volume was subjected to the action of UV light for 60 min. The dye removal efficiency was around 91.43%.

3.5. Adsorption of BBG with the nanocomposite

The adsorption experiment was carried out in the presence of the nanocomposite under the same conditions of photocatalytic removal. The results are illustrated in Fig. 6 and Table 3. The adsorption removal of BBG dye reached 66.44% [20].

4. Conclusions

The photocatalytic and adsorption removals of BBG dye from the nanocomposite depend on the dosage of the nanocomposite, pH value, and reaction temperature. The photocatalytic removal under the UV illumination of BBG dye reached 91.43%, this result is better than the adsorption removal that has reached 66.44%, by using the prepared MWCNTs/MO with pH = 5, nanocomposite dosage of 0.03 gm/L, temperature of 30 °C with 50 ppm of the dye solution, and the illumination time is 60 min.

1. T. Masciangioli, W.X. Zhang. Peer reviewed: Environmental technologies at the nanoscale. *Envir. Sci. Tech.* **37**, 102A (2003).
2. E. Roduner. Size matters: Why nanomaterials are different. *Chem. Soc. Rev.* **35**, 583 (2006).
3. C. Darnault, K. Rockne, A. Stevens, G.A. Mansoori, N. Sturchio. Fate of environmental pollutants. *Water Environment Res.* **77**, 2576 (2005).
4. G.A. Mansoori, T.R. Bastami, A. Ahmadpour, Z. Eshaghi. Environmental application of nanotechnology. *Ann. Rev. Nano Res.* **2**, 1 (2008).
5. D. Grosso, F. Cagnol, G.D.A. Soler-Illia E.L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau A. Bourgeois, C. Sanchez. Fundamentals of mesostructuring through evaporation-induced self-assembly. *Advanced Funct. Mater.* **14** (4), 309 (2004).
6. C.A. Furtado, U.J. Kim, H.R. Gutierrez, L. Pan, E.C. Dickey, P.C. Eklund. Debundling and dissolution of single-walled carbon nanotubes in amide solvents. *J. Am. Chem. Soc.* **126**, 6095 (2004).
7. M.J. O'Connell, S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J.P. Ma, R.H. Hauge, R.B. Weisman, R.E. Smalley. Band gap fluorescence from individual single-walled carbon nanotubes. *Science.* **593**, 297 (2002).
8. M. Monthieux, B.W. Smith, B. Bouteaux, A. Claye, J.E. Fischer D.E. Luzzi. Sensitivity of single-wall carbon nanotubes to chemical processing: an electron microscopy investigation. *Carbon.* **39**, 1251 (2001).
9. B.I. Yakobson, C.J. Brabec, J. Bernholc. Nanomechanics of carbon tubes: Instabilities beyond linear response. *Phys. Rev. Lett.* **76**, 2511 (1996).
10. V.K. Gupta, S. Agarwal, T.A. Saleh. Synthesis and characterization of alumina coated carbon nanotubes and their application for lead removal. *J. Hazardous Mater.* **185**, 17 (2011).
11. S. Wang, X. Shi, G. Shao, X. Duan, X. Yang, X. Wang. Preparation, characterization and photocatalytic activity of multi-walled carbon nanotube-supported tungsten trioxide composites. *J. Phys. Chem. Sol.* **69**, 2396 (2008).

12. D.W. Lee, J.W. Seo. sp²/sp³ carbon ratio in graphite oxide with different preparation times. *J. Phys. Chem. C* **115**, 2705 (2011).
13. Y.J. Xu, Y. Zhuang, X. Fu. New insight for enhanced photocatalytic activity of TiO₂ by doping carbon nanotubes: A case study on degradation of benzene and methyl orange. *J. Phys. Chem. C* **114**, 2669 (2010).
14. E.J. Mohammad, M.M. Kareem, A.J. Atiyah. Removal of dye bismarck brown G by photocatalytic reaction over prepared co-oxide Cr₂O₃-NiO: A kinetic study. *Asian J. Chem.* **30**, 2527 (2018).
15. C. Kao, R. Young. A Raman spectroscopic investigation of heating effects and the deformation behavior of epoxy/SWNT composites. *Composites Sci. Tech.* **64**, 2291 (2004).
16. S. Costa, E. Palen, M. Kruszynsky, A. Bachmatiuk, R. Kalenczuk. Characterization of carbon nanotubes by Raman spectroscopy. *Mater. Sci.-Poland* **26**, 2 (2008).
17. D.A. Skoog, F.J. Holler, S.R. Crouch. *Principles of Instrumental Analysis* (Thomson Brooks/Cole, 2007).
18. A. Yildirim, T. Seçkin. In situ preparation of polyether amine functionalized MWCNT nanofiller as reinforcing agents. *Advances in Mater. Sci. Eng.* ID 356920, 1 (2014).
19. S.K. Anshul, M. Aman, R.K. Bedi, K. Subodh, A.K. Debnath, D.K. Aswald. CNTs based improved chlorine sensor from noncovalently anchored multi-walled carbon nanotubes with hexa-decafluorinated cobalt phthalocyanines. *RSC Adv.* **7**, 49675 (2017).
20. K.I. Falk, B.A. Coasne, R.J.M. Pellenq. Effect of temperature on adsorption of mixtures in porous materials. *Mol. Simul.* **40**, 45 (2014).

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СИНТЕЗ ВУГЛЕЦЕВИХ НАНОТРУБОК
З ГРАФІТУ ТА ДОСЛІДЖЕННЯ КАТАЛІТИЧНОЇ
АКТИВНОСТІ КОМПЗИТУ МWCNTs/Cr₂O₃-NiO
З ВИДАЛЕННЯМ КОРИЧНЕВОГО БАРВНИКА
БІСМАРК Г З ЙОГО ВОДНОГО РОЗЧИНУ

Резюме

Описано синтез вуглецевих нанотрубок з графіту методом хімічного осадження та нанокомпозитів з багатостінних вуглецевих нанотрубок (БСВН) і нанокомпозита БСВН/МО(Cr₂O₃-NiO) із застосуванням випаровування і висушування. Композити досліджені методами дифракції рентгенівських променів, фур'є-перетворення інфрачервоних спектрів і раманівської спектроскопії. Активність композитів визначена з видаленням коричневого барвника Бісмарк Г з водного розчину реакціями фотокаталізу. Ефективність видалення дорівнює 91,43% після реакції протягом 1 години при оптимальних умовах (маса 0,03 г, рН = 5 і температура 30 °C).