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THE STUDY OF ADSORPTION OF ANTHRACENE ONTO PMMA-FUNCTIONALIZED MWCNTS AND PRISTINE MWCNTS BY FLUORESCENCE SPECTROSCOPY TECHNIQUE

Umit Ay[1,*], Murat Isik[2], Nergis Arsu[2]

[1]Department of Chemistry, Kocaeli University, 41380, Kocaeli, Turkey
[2]Department of Chemistry, Yildiz Technical University, 34220, Istanbul, Turkey

ABSTRACT

Adsorption of anthracene as polycyclic aromatic hydrocarbon molecule on the pristine multi-walled carbon nanotubes (MWCNTs) and functionalized MWCNTs with polymethyl methacrylate (PMMA) has been investigated in an attempt to explore adsorption mechanisms. The morphology of MWCNTs was observed by a Scanning Electron Microscope. Thermal Gravimetric Analysis was used to obtain the degree of polymer functionalization of MWCNTs after the thermal polymerization of Methyl methacrylate (MMA) with benzoylperoxide. Changing of fluorescence intensity as a function of time is recorded to follow the variance of adsorption.

KEYWORDS:
Carbon nanotubes; Luminescence; Anthracene; Adsorption

INTRODUCTION

Carbon nanotubes (CNTs)have a wide field of industrial applications and have also used as adsorbent in water treatment and environmental pollution [1-5]. CNTs have also attracted attention due to their excellent optical activity and mechanical strength. Although there are some studies on the adsorption of organic pollutants by carbon nanotubes [6-12]. So far, there are no studies showing systematically the adsorptive interaction between CNTs and polycyclic aromatic hydrocarbons (PAHs). Therefore, it is very important to understand the interaction between the carbon nanotubes and organic pollutants. CNTs and organic chemicals are expected to have strong interactions due to their hydrophobic surfaces.

There are numerous studies about the adsorbent efficiency of CNTs for organic chemicals [13-18]. This strong interaction effectively alters the mobility, bioavailability and environmental risk of organic chemicals. Polycyclic aromatic hydrocarbons (PAHs) are found in organic substances, incomplete burning of fuels, coal tar and bitumen. The distribution of PAHs in the environment is extensive since they are found in air, soil and water. PAHs can be classed as carcinogenic and/or genotoxic chemical. Therefore, the determination of PAHs is very important [19]. CNTs are considered to be a good choice to study the adsorption mechaenism. Understanding adsorptive interactions between organic contaminants and CNTs is critical to both the environmental application as special adsorbents and the assessment of the potential impact on the fate and transport of organic contaminants in the environment.

In this study, functionalization of MWCNTs via thermal polymerization of methyl methacrylate (MMA) with benzoyl peroxide was achieved to help to reduce the solubility problem of MWCNTs. Since anthracene is a good candidate among PAHs. Adsorption of anthracene studies were performed by using both polymer (PMMA) functionalized MWCNTs and pristine MWCNTs and the percentage of adsorption was determined by fluorescence spectroscopy.

MATERIALS AND METHODS

Functionalization of MWCNTs via Thermal Polymerization of MMA. 46.8 mg MWCNTs was suspended in 50 ml of toluene and 50 ml MMA was added to this solution. 24.2 mg benzoyl peroxide as an initiator was added to this mixture under nitrogen atmosphere and was refluxed in an oil bath at 85°C for 5 days. After completion of the reaction, the PMMA functionalized MWCNT was extracted by THF.

Adsorption experiments. Composite solutions for the adsorption experiments were prepared by using MWCNTs/anthracene in a 1:1 ratio by weight (w/w). 9.4 mg anthracene was dissolved in 5 ml of toluene and 9.4 mg of either MWCNTs or PMMA-MWCNTs was added to this solution.

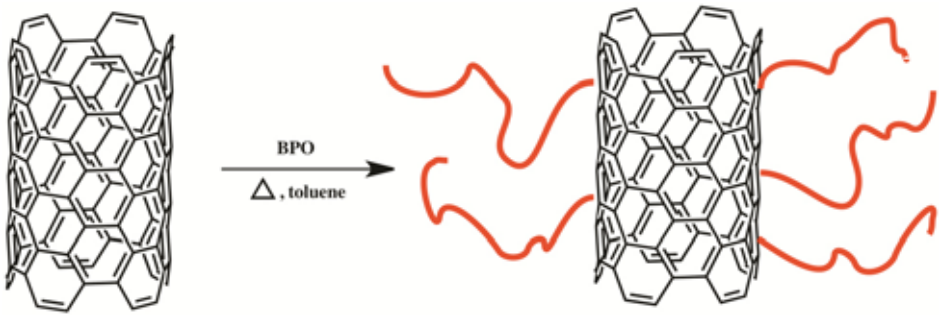
The solutions of anthracene and MWCNTs/ PMMA-MWCNTs were sonicated using a sonic tip (Ultrasonic processor VCX 500 W) for 3x10 s at

26% of the power output. If the sonication treatment is too aggressive and/or too long, MWCNTs can be easily and seriously damaged, especially when a probe sonicator is employed. The suspensions were allowed to settle down starting from 5 min up to 121 h. All the dispersions were centrifuged at 3000 rpm for 60 min and then the suspensions were used depending on the time variations to determine the adsorption properties by fluorescence spectroscopy (Jobin Yvon-Horiba Fluoromax-P).

RESULTS AND DISCUSSION

Functionalization of the MWCNTs was achieved by bulk polymerization of MMA with benzoylperoxide (BPO) at 85°C as depicted in Scheme 1.

The degree of functionalization was determined by TGA (see Fig. 1).



SCHEME 1

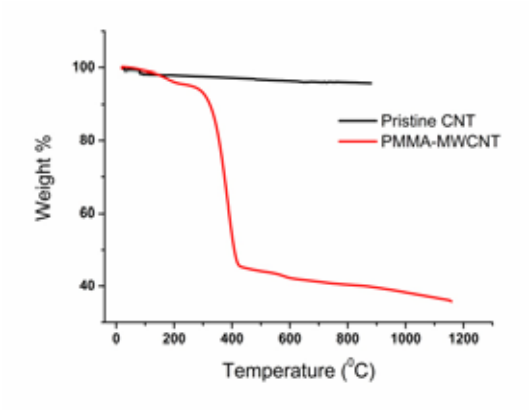


FIGURE 1
TGA curves of pristine MWCNTs and PMMA-MWCNTs

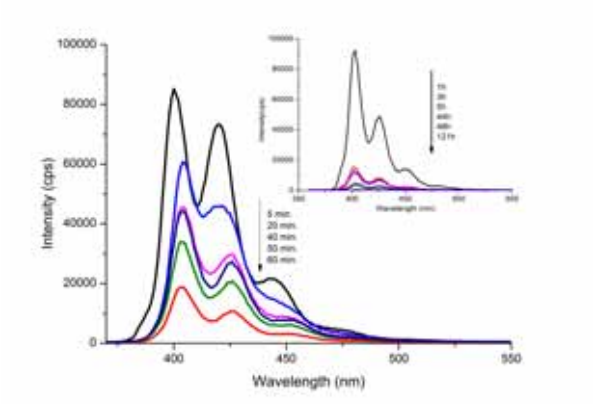


FIGURE 2
Fluorescence emission spectra of solutions of PMMA-MWCNTs/Anthracene/Toluene for various time intervals; λ_{exc} = 350 nm.
(Inset: Prolonged adsorption results)

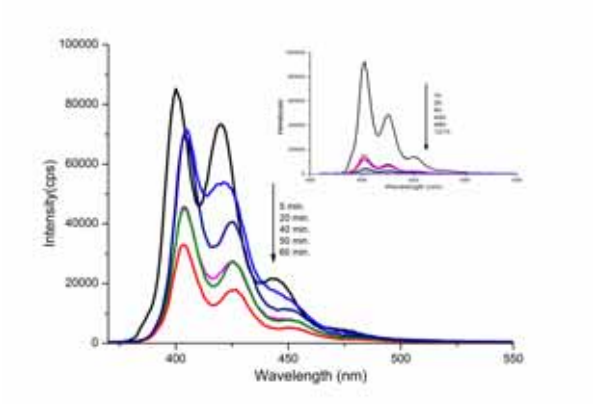


FIGURE 3
Fluorescence emission spectra of solutions of Pristine-MWCNT/Anthracene/Toluene for various time intervals; λ_{exc} = 350 nm.
(Inset: Prolonged adsorption results)

PMMA functionalization was found to be 58% from the TGA curves for PMMA-MWCNTs. Functionalization of MWCNTs is necessary since dispersing them is very difficult as CNTs have large surface areas and van deer Waals' forces.

There are numerous studies about obtaining homogenous and the fine dispersion of CNTs and one of them is the introduction of functional groups onto the CNT surface [7-10]. PMMA- attached MWCNTs have been useful to improve their dispersion properties and this factor will possibly play a good role for investigation of the adsorption properties of anthracene as a polyaromatic hydrocarbon. Since polyaromatic hydrocarbons are good luminescents, in this study anthracene was used as a chromophore label for detecting adsorption onto both PMMA-functionalized MWCNTs and pristine MWCNTs by the fluorescence technique.

To determine the percentage of adsorption from the changes, fluorescence emission spectra were recorded while the solutions were excited at λ = 350 nm. The results are shown in Figs.2 and 3 for the experiments performed on both MWCNTs.

The addition of either PMMA-MWCNTs or pristine-MWCNTs to the solutions in a 1:1 ratio by weight results in a visible quenching of the anthracene fluorescence emission even after 5 minutes of duration (see Figs 2 and 3).

The quenching of the fluorescence gives a strong indication that an interaction is occurring between the CNTs and the anthracene molecule.

The results obtained from the fluorescence measurements recording the changes of emission spectra of the anthracene molecules in the presence of the CNTs are tabulated in Table 1.

TABLE 1
Changes of emission intensity of PMMA-MWCNTs and Pristine-MWCNTs

	Changes of emission intensity %	
Time (mins.)	**PMMA-MWCNT**	**Pristine-MWCNT**
5	29	16
20	46	18
40	48	46
50	60	47
60	78	61
180	86	81
300	88	86
2640	96	96
7260	99	99

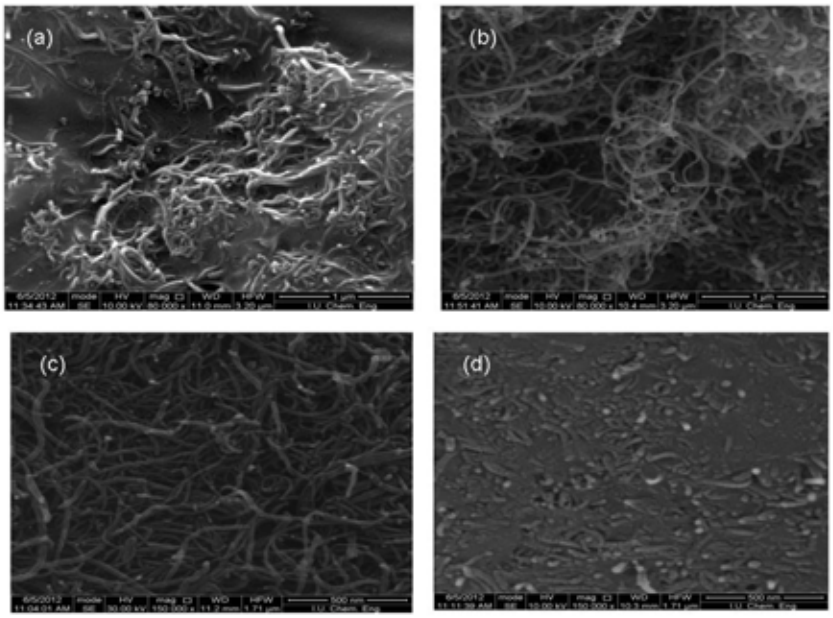


FIGURE 4
Representative SEM images of (a) pristine MWCNTs, (b) PMMA modified MWCNTs, (c) pristine MWCNT with anthracene, (d) PMMA modified MWCNTs with anthracene

As can be seen from Table 1, the adsorption of anthracene onto the PMMA attached MWCNTs is nearly 30% while 16% adsorption was obtained when the pristine MWCNTs were used. During the 1 hour of duration, the adsorption of anthracene increased to 78% for the PMMA-MWCNTs and 61% for the pristine MWCNTs.

The results are not differentiated for the prolonged adsorption times of either CNTs (99% for both CNTs during 121 hours (7260 mins)). The adsorption of functionalized MWCNTs is much better than the pristine MWCNTs, especially in a short period of time. Possibly, the functional groups can change the wettability of the CNT surfaces, and consequently make the CNTs more hydrophilic and thus more suitable for the adsorption of relatively low molecular weight and polar compounds [6].

As reported in the literature [6], five possible interactions are responsible for the adsorption of organic chemicals onto the CNT surface. These are: the hydrophobic effect, Π- Π bonds, hydrogen bonds and covalent and electrostatic interactions. Π-Π bonding interactions between the organic molecules and CNTs were also demonstrated by spectroscopic techniques [20-26].

Beside CNT-organic chemical interactions, polymeric adsorbents have been developed and used for the removal of organic chemicals from solutions. As reported previously, introducing some special functional groups into the chemical structure of the polymer helps to improve its adsorption capacity towards specific organic compounds. Therefore, the one-component structure of PMMA-attached MWCNTs presented combined effects such as the enhancement of the specific area and modification of the surface properties.

Adsorption of Anthracene onto MWCNTs remarkably increased when the MWCNTs were chemically functionalized. This is as a result of the surface area as well as the porosity of PMMA. Obviously functionalization of the MWCNTs produced a strong interfacial bond with other chemicals.

Fig.4 presents SEM microphotographs; pristine MWCNTs (Fig. 4a), PMMA attached MWCNTs (Fig. 4b), adsorption of anthracene onto MWCNTs (Fig. 4c) and adsorption of anthracene onto PMMA attached MWCNTs (Fig. 4d), respectively. Fig. 4a presents curled and entangled shaped pristine MWCNTs. After the attachment of the polymer it is easy to see the agglomeration. Fig. 4c and Fig. 4d show SEM microphotographs of MWCNTs and PMMA-MWCNTs after anthracene adsorption.

CONCLUSION

As was expected, the adsorption of anthracene with PMMA functionalized MWCNTs is very fast and 50% is completed after 20 mins. In contrast, with pristine-MWCNT the adsorption process is much slower; just 18% change was obtained in a similar time interval. A large surface area and possibly the porosity of the polymer functionalized MWCNTs provides enough adsorption sides for the anthracene.

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REFERENCES

[1] Rao, G.P., Lu, C. and Su, F. (2007) Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review, Sep. Purif. Technol. 58, 224-231.

[2] Liao, Q., Sun, J. and Gao, L. (2008) The adsorption of resorcinol from water using multiwalled carbon nanotubes, Colloid Surf. A 312, 160-165.

[3] Tofighy, M.A. and Mohammadi, T. (2011) Adsorption of divalent heavy metal ions from water using carbon nanotube sheets, J. Hazard. Mater.185, 140-147.

[4] Li, Y.H., Ding, J., Luan, Z.K., Di, Z.C., Zhu, Y.F. Xu, C.L. Wu, D.H. and Wei, B.Q. (2003) Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 41, 2787-2792.

[5] Tian, X.L., Zhou, S., Zhang, Z.Y., He, X.A. Yu, M.J. and Lin, D.H. (2010) Metal impurities dominate the sorption of a commercially avai-lable carbon nanotube for Pb(II) from water, Environ. Sci. Technol. 44, 8144-8149.

[6] Pan, B. and Xing, B.S. (2008) Adsorption mechanisms of organic chemicals on Carbon Nanotubes, Environ. Sci. Technol. 42, 9005-9013.

[7] Debnath, S., Cheng, Q., Hedderman, T.G., Byrne, HJ. (2008) A study of the interaction between single-walled carbon nanotubes and polycyclic aromatic hydrocarbons: Toward structure-property relationships, Phys. Chem. C 112, 10418-10422.

[8] Chen, W., Duan, L., Zhu, D.Q. (2007) Adsorption of polar and nonpolar organic chemicals to carbon nanotubes, Environ. Sci. Technol. 41, 8295-8300.

[9] Chen, W., Duan, L., Wang, L.L. and Zhu, D.Q. (2008) Adsorption of hydroxyl- and amino-substituted aromatics to carbon nanotubes, Environ. Sci.Technol. 42, 6862-6868.

[10] Cho, H.H., Smith, B.A., Wnuck, J.D., Fairbrother, DH. and Ball, W.P. (2008) Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nano-tubes, Environ. Sci. Technol. 42, 2899-2905.
[11] Lin, D.H. and Xing, B.S. (2008) Adsorption of phenolic compounds by carbon nanotubes: Role of aromaticity and substitution of hydroxyl groups, Environ. Sci. Technol. 42, 7254-7259.
[12] Wang, X.L., Tao, S. and Xing, B.S. (2009) Sorption and competition of aromatic compounds and humic acid on multiwalled carbon nanotubes, Environ. Sci. Technol. 43, 6214-6219.
[13] Wesolowski, RP., Furmaniak, S., Terzyk, A.P. and Gauden, P.A. (2011) Simulating the effect of carbon nanotube curvature on adsorption of polycyclic aromatic hydrocarbons, Adsorption 17, 1-4.
[14] Zhang, J., Lee, J.K., Wu, Y. and Murray, R.W. (2003) Photoluminescence and electronic interaction of anthracene derivatives adsorbed on sidewalls of single-walled carbon nano-tubes, Nano lett. 3 403-407.
[15] Ma, C., Zhang, W., Zhu, Y.F., Li, L.J., Zhang, R.P., Koratkar, N. and Liang, J. (2008) Alignment and dispersion of functionalized carbon nanotubes in polymer composites induced by an electric field, Carbon 46, 706-710.
[16] Ma, P.C., Siddiqui, N.A., Marom, G. and Kim, J.K. (2010) Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review, Composities: Part A 41, 1345-1367.
[17] Jia, Z.J., Wang, Z.Y., Xu, C.L., Liang, J., Wei, B.Q., Wu, D.H. and Zhu, S.W. (1999) Study on poly(methyl methacrylate)/carbon nanotube composites, Mater. Sci. Eng. A 271, 395-400.
[18] Park, S.J., Cho, M.S., Lim, S.T., Choi, H.J., Jhon, M.S. (2003) Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with poly(methyl methacrylate) prepared by in-situ bulk polymerization, Macromol. Rapid Commun. 24, 1070-1073.
[19] Alarcon, F., Baez, M.E., Bravo, M., Richter, P., Escander, G.M., Olivieri, A.C. and Fuantes, E. (2013) Feasibility of the determination of polycyclic aromatic hydrocarbons in edible oils via unfolded partial least-squares/residual bilinearization and parallel factor analysis of fluorescence excitation emission matrices, Talanta 103, 361-370.
[20] Chen, J., Liu, H.Y., Weimer, W.A., Halls, M.D., Waldeck, D.H. and Walker, G.C. (2002) Noncovalent engineering of carbon nanotube surfaces by rigid, functional conjugated poly-mers, J. Am. Chem. Soc. 124, 9034-9035.
[21] Chen, J.Y., Chen, W. and Zhu, D. (2008) Adsorption of nonionic aromatic compounds to single-walled carbon nanotubes: Effects of aqueous solution chemistry, Environ. Sci. Technol. 42, 7225-7230.
[22] Star, A., Stoddart, J.F., Steuerman, D., Diehl, M., Boukai, A., Wong, E.W., Yang, X., Chung, S.W., Choi, H. and Heath, J.R. (2001) Preparation and properties of polymer-wrapped single-walled carbon nanotubes, Angew. Chem. Int. Ed. 40, 1721-1725.
[23] Zhao, J.J., Lu, J.P., Han, J. and Yang, C.K. (2003) Noncovalent functionalization of carbon nanotubes by aromatic organic molecules, Appl. Phys. Lett. 82, 3746-3748.
[24] Woods, L.M., Badescu, S.C. and Reinecke, T.L. (2007) Adsorption of simple benzene derivatives on carbon nanotubes, Phys. Rev. B 75, 155415.
[25] Gotovac, S., Honda, H., Hattori, Y., Takahashi, K., Kanoh, H. and Kaneko, K. (2007) Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons, Nano lett. 7, 583-587.
[26] Gotovac, S., Yang, C.M., Hattori, Y., Takahashi, K., Kanoh, H. and Kaneko, K. (2007) Adsorption of polyaromatic hydrocarbons on single wall carbon nanotubes of different functionalities and diameters, J. Colloid. Interface Sci. 314, 18-24.

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CORRESPONDING AUTHOR

Umit Ay
Department of Chemistry,
Kocaeli University,
41380, Kocaeli – TURKEY

e-mail: umurege@kocaeli.edu.tr