CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216
DOI: 10.3303/CET2186059

Efficient Removal of Cationic and Anionic Dyes from Wastewater using Carbon Nanotubes from Petrochemical Waste Oil

Ramiro Emerson C. Amon[a], Chosel P. Lawagon[b,*]

[a]Chemical Engineering Department, College of Engineering Education, University of Mindanao, Davao City, Philipines
[b]Professional Schools, University of Mindanao, Davao City, Philippines
ramiro_amon@umindanao.edu.ph

Dye-contaminated wastewater from the textile industry and petrochemical waste oil (PWO) constitute a very serious threat to the environment. The presence of dyes in water inhibits penetration of sunlight, decreasing the photosynthetic processes of aquatic plants, resulting in the disruption of aquatic ecosystems. Moreover, organic dyes are known to have adverse effects on the human health, which presents a risk to the sources of clean drinking water. On the other hand, petrochemical waste oil is difficult to degrade and contains heavy metals and harmful additives. When dumped on landfills, waste oil may seep through the soil and find its way to bodies of water. Recycling technologies are still underdeveloped, and treatment proves to be expensive. Thus, it is crucial to improve the alternative upcycling technology of petrochemical waste oil. Herein, carbon nanotubes (CNT) were synthesized from PWO by simple catalytic vapor deposition (CVD). These CNTs were then used for systematic study on the removal of cationic and anionic dyes from wastewater. Dye removal by the as-synthesized CNT was Langmuir-type adsorption and followed the pseudo-second-order rate model for both the cationic and anionic dyes. Factors like solid-to-liquid ratio, initial dye concentration, and removal efficiency were investigated. CNT from PWO showed a relatively short adsorption time of less than an hour (t~60 min) for both types of dye and demonstrated very high dye adsorption capacities (q_m). Hence, this study opens the possibility of using the PWO-derived CNT for large-scale dye-contaminated wastewater treatment.

1. Introduction

The rapid industrialization of the world over the past century has left adverse effects on the environment. One of the most significant contributors to water pollution is the textile industry, which contributes around 20% of industrial water pollution, equivalent to about 10,000 metric tons of industrial dye every year (Wong et al., 2020). Dye contamination in natural bodies of water affects the water's aesthetics, chemical properties, and habitability to aquatic life forms. Wastewater from the textile industry has relatively high BOD and COD, which are greatly attributed to the non-biodegradable organic dyes (Lellis et al., 2019). Being clearly visible, the presence of dyes inhibits sunlight from penetrating bodies of water and thus disrupt photosynthesis and the aquatic ecology in general (Yaseen & Scholz, 2019). In addition, trace amounts of dyes in water are also reported to cause skin irritation. They are also found to be carcinogenic and mutagenic to humans and other aquatic life forms (Lellis et al., 2019).

A lot of treatment technologies have been studied and applied for the removal of dyes from water, including coagulation, flocculation (Wong et al., 2020), electrochemical techniques, and membrane separation (Hossen et al., 2019). Yet despite such advancements in treatment technologies, finding cost-effective and rapid water treatment method at an industrial level still poses a challenge (Duman, Tunç, Polat, & Bozoğlan, 2016). On the other hand, adsorption technology has been studied previously and has been found to be effective in handling large amounts of wastewater and produces a relatively high-quality effluent. It is one of the most effective methods employed by industries to treat hazardous pollutants present in wastewater. This type of treatment technology does not produce harmful by-products, such as free radicals and ozone (Duman et al., 2019).

Paper Received: 13 September 2020; Revised: 21 February 2021; Accepted: 7 May 2021
Please cite this article as: Amon R.E., Lawagon C.P., 2021, Efficient Removal of Cationic and Anionic Dyes from Wastewater Using Carbon Nanotubes from Petrochemical Waste Oil, Chemical Engineering Transactions, 86, 349-354 DOI:10.3303/CET2186059

Treatment of dye-contaminated wastewater was done using different adsorbents such as inorganic minerals (Dai et al., 2018), carbon-based materials (e.g., activated carbon, carbon nanotubes, graphene) (Abdi et al., 2017), and biomass-derived carbon materials (Jin et al., 2018). However, carbon nanotubes (CNTs) have been gaining a lot of attention in water treatment because of their excellent properties as adsorbents (AlOmar et al., 2017). Carbon nanotubes have been a subject of extensive research because of their unique physicochemical properties (Homayoon et al., 2017). They are characterized by high surface area and adsorption capacity, good mechanical stability, high chemical purity, and thermal and chemical stability, which are ideal adsorption materials (Rajabi et al., 2017).

Another environmental concern is waste petrochemical oil (PWO), which is generated at around 24 million metric tonnes per year (Abdullah et al., 2020). These wastes have detrimental effects on the environment and human health because of their heavy metal contents and the presence of additives, including phenols, aromatic hydrocarbons, and compounds containing zinc, chlorine, or phosphorous (Maceiras et al., 2017). There is a need, therefore, to upcycle these waste oils. One method of which is its utilization as a raw material for CNT synthesis through catalytic vapor decomposition (CVD). CVD is a simple and cost-effective method for this type of application which produces high-purity CNT's under controlled conditions(Venkatesan et al., 2018). It is environmentally benign as it produces negligible amounts of harmful by-products (Plata et al., 2009).

This study will provide an alternative adsorbent material to conventional activated carbon and other commercial adsorbents for dyes if proven effective. It will also offer a value upgrade for petrochemical waste oils that require expensive treatment for waste disposal and recycling. Ultimately, this study aims to mitigate the pollution caused by the presence of industrial dyes in bodies of water.

This research paper's primary objective is to synthesize CNTs from PWO and utilize it as an adsorbent for the removal of cationic and anionic dyes. Optimum adsorption conditions shall be determined by establishing the kinetics, isotherms, effects of adsorbent dosage and pH, and recyclability.

2. Experimental Section

2.1 Materials

The carbon nanotubes were synthesized by catalytic vapor deposition (CVD). Dyes used for the adsorption experiments were Methylene blue (MB, $C_{16}H_{18}ClN_3S$, MW=319.85, $\lambda_{max} = 664\ nm$) for cationic dyes and Methyl Orange (MO, $C_{14}H_{14}N_3NaO_3S$, MW=327.33, $\lambda_{max} = 465\ nm$) for anionic dyes. Both were manufactured by Scharlau chemicals (European Union). All the chemicals used were as packaged.

2.2 Carbon Nanotubes Synthesis

PWO was vaporized at around 930 ˚C. The carbon precursor and catalyst for the formation of CNTs were hypofluorous acid (HFO) and ferrocene, present in a 1:10 molar ratio, while nitrogen gas was used as the carrying medium at 100 cm^3/h. The carbon nanotubes formed were refined using hydrogen peroxide and hydrochloric acid at a 2:1 (v/v) ratio and sonicated for 5 hours at 60 ˚C.

2.3 Carbon Nanotubes Synthesis

The adsorption characteristics of the as-produced CNTs were evaluated at different contact time, initial dye concentration, initial pH, and adsorbent-solution ratio to determine the adsorption kinetics, isotherm, and optimum operating conditions. Each trial for the adsorption experiments was done at room temperature. CNTs were mixed with a certain amount of dye-contaminated water (V) and agitated (150 rpm) at a given amount of time (t). The concentration at any time, C_t, and the equilibrium concentration, C_e, will be determined analytically. Removal efficiency (%RE, Eq. 1) (Ibrahim et al., 2019) and adsorption capacity (q_e, Eq. 2) (Choi & Yu, 2018) at equilibrium determined were calculated taking into account the amount of CNT adsorbent (m).

$$\%RE = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

Determination of adsorption kinetics was done by measuring the dye uptake (q_t, Eq.3) (Menkiti et al., 2018) of the carbon nanotubes using an initial dye concentration of 20 mg/L.

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{3}$$

This was done at different adsorption time (t) until equilibrium is achieved. The initial concentration for the determination of the adsorption isotherm was varied between 5 – 200 mg/L, and the effect of the adsorbent dosage and was investigated by varying the solid-liquid ratio (S/L) between 0.5 – 2.0 g/L.

2.4 Analytical Methods

Measurement of the solution concentrations was done using a UV-Visible spectrophotometer (Shimadzu UV-VIS: UV-MINI1240, Japan). Calibration curves relating absorbance and dye concentration for methylene blue and methyl orange were generated by measuring the absorbance of the solutions of known concentrations (1.0 – 200 mgL-1).

3. Results and discussions

3.1 Characterization

To understand its morphology, SEM micrographs of the synthesized CNTs from PWO after purification were obtained as shown (Figure 1a). The developed CNTs were clean and nonporous with long, tangled, and randomly curved geometry. Edges appear to be smooth, and only small traces of impurities are observed. On the other hand, BET analysis gives a specific surface area of 133.47 m^2g^{-1} (Figure 1b).

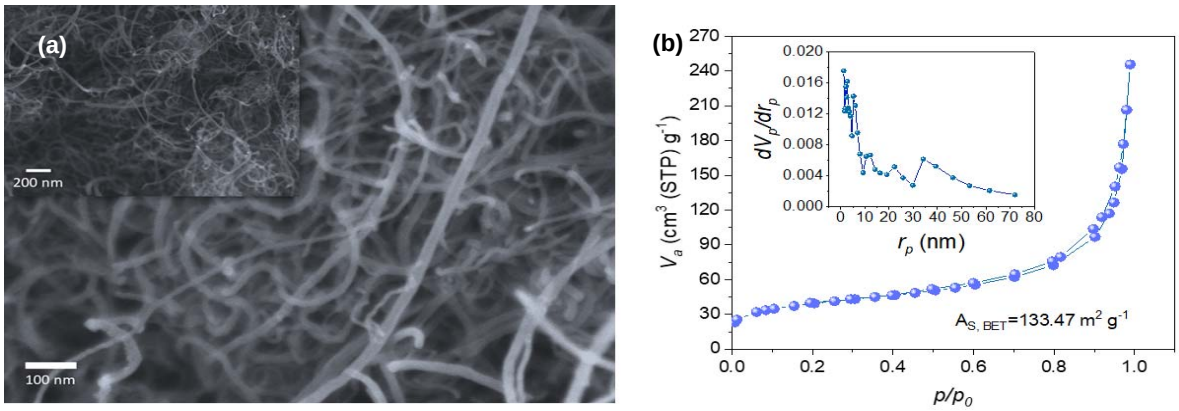

Figure 1: (a) SEM image of purified CNT from PWO and (b) N_2 adsorption-desorption isotherms with BJH plot

XRD spectra (Figure 2a) exhibits crystallinity of the produced CNT with a diffraction peak at 26.1° ascribed to the graphite plane (002) reflection, which are attributed to the graphitic carbon of multi-walled CNT (Sa et al., 2018). The Raman spectra (Figure 2b) revealed distinct peaks of D (~1341 cm^{-1}), G (~1571 cm^{-1}), and 2D (~2683 cm^{-1}) bands attributed to surface defects, graphitic carbon, and overtone of D band respectively (Price et al., 2018).

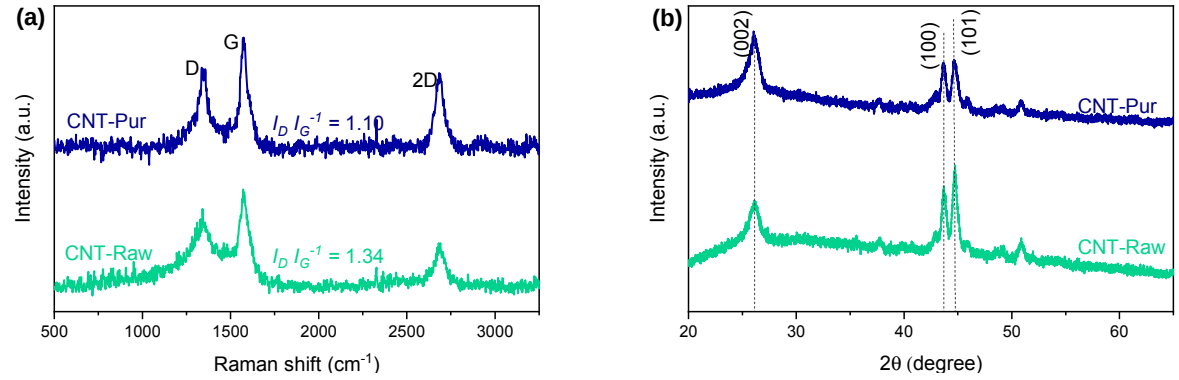

Figure 2: (a) XRD and (b) Raman spectra of raw and purified CNT from PWO

3.2 MB and MO Adsorption Mechanism in CNT from PWO

Dye's uptake mechanism onto as-synthesized CNTs were explored to understand its optimal adsorptive behavior.

3.2.1 MB and MO Adsorption Kinetics and Isotherm

Dye uptake of the synthesized CNTs is extremely fast for both MB and MO for the first 10 minutes (~99%), which can be attributed to the high specific surface area available for adsorption. The removal efficiency plateaued from 10 minutes onward until reaching equilibrium. Nonlinear regression analyses of the MB and MO uptake mechanism of CNTs were done using first-order (Eq. 5) and second-order (Eq. 6) models (Kang S.B. et al., 2020).

$$q_t = q_e(1 - e^{-k_1 t}) \tag{5}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{6}$$

Results (Figure 3) show that both follow a pseudo second-order adsorption kinetics. This suggests that chemisorption (Xiong et al., 2018) occurs and that the adsorption rate depends on the availability of adsorption sites on the surface of CNTs rather than the number of adsorbed MB and MO dye molecules (Choi & Yu, 2018).

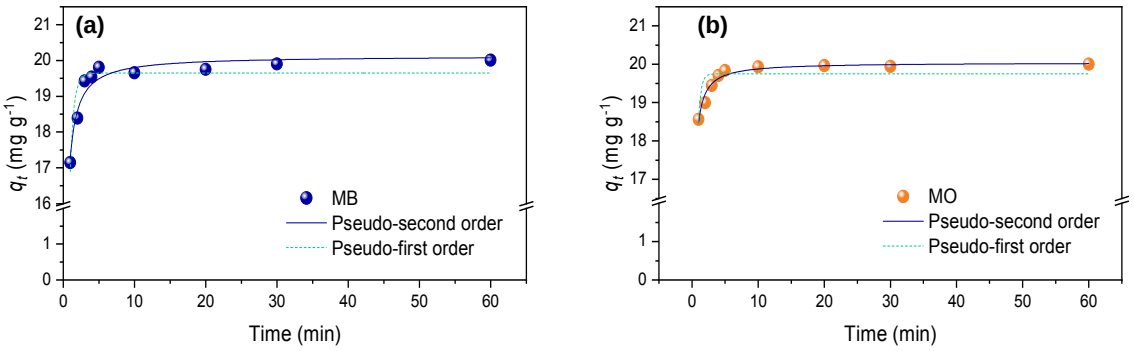

Figure 3: Time profile and kinetic model fitting of (a) MB and (b) MO adsorption in CNT at Co = 20 mgL^{-1}, pH = 7, S/L ratio = 0.1 gL^{-1}, V = 25 mL, and T = 25 °C.

Table 1: Kinetic parameters for MB and MO adsorption in CNT from PWO

	Pseudo-first order			Pseudo-second order		
Dye	q_e (mg g^{-1})	k_1 x 10^{-2} (min^{-1})	r^2	q_e(mg g^{-1})	k_2 x 10^{-3} (g mg^{-1} min^{-1})	r^2
Methylene Blue	16.65	1.96	0.84344	20.13	4.66	0.94161
Methyl Orange	19.75	2.24	0.63932	20.05	11.71	0.95513

Investigation of the adsorption isotherms was done using nonlinear regression of Langmuir (Eq. 7) and Freundlich (Eq. 8) models (Menkiti et al., 2018).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

$$q_e = K_F C_e^{1/n} \tag{8}$$

From the results (Figure 4), the Langmuir isotherm best describes the equilibrium adsorption of both MB and MO in CNT, which suggests that a monolayer of dye molecules is formed at the adsorbent surface and that the surface is homogeneous (Duman et al. , 2016). Isotherm constants are summarized in Table 2.

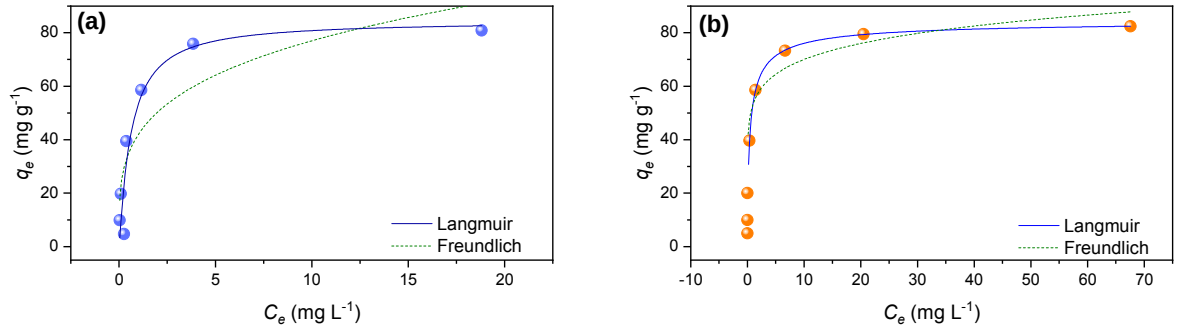

Figure 4: Adsorption Isotherms of (a) MB and (b) MO in CNT

Table 2: Adsorption isotherm constants

	Langmuir			Freundlich		
Dye	q_m (mg g^{-1})	K_L (L mg^{-1})	r^2	n	K_F (L g^{-1})	r^2
Methylene Blue	84.44	1.71	0.89780	3.78	41.91	0.77523
Methyl Orange	85.04	1.72	0.99993	8.44	53.32	0.87707

3.2.2 Effect of Adsorbent Dosage

As the amount of adsorbent increases per unit volume of solution, the active site for adsorption increases resulting in higher removal percentage. However, the increase in removal efficiency became negligible at higher adsorbent dosage (1.0 gL^{-1}) for both MB and MO, as shown in Figure 5.

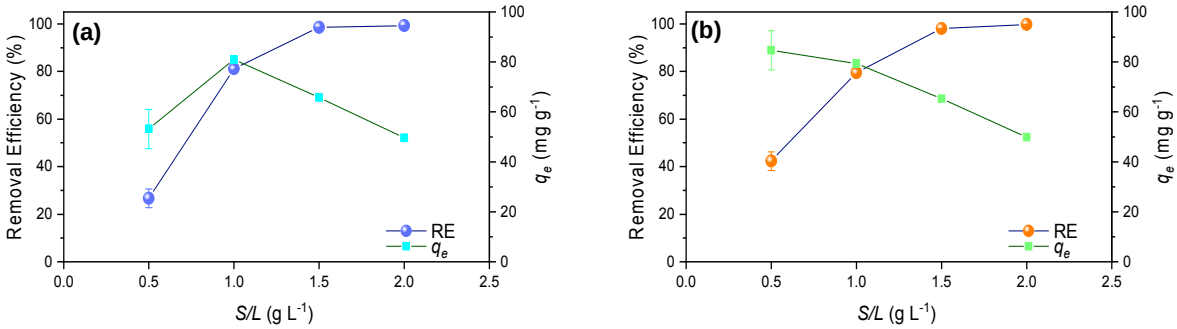

Figure 5: Effect of dosage for (a) MB and (b) MO in CNT at C_o = 100 mgL^{-1}, pH = 7.0, and T = 25 °C

4. Conclusions

Upcycling of petrochemical waste oil to carbon nanotubes offers a promising adsorbent for cationic and anionic dyes reaching q_m of around 85 mg g^{-1}. The dye uptake follows a Langmuir-type isotherm and a pseudo-second order rate of adsorption. Its adsorption rate is relatively fast (~60 min) owing to its large specific surface area. It has a very high potential application for varying or mixed dye contaminated wastewater as it can adsorb both cationic and anionic dyes.

Acknowledgement

This study was funded by the Research and Publication Center of the University of Mindanao under the Dolores P. Torres (DPT) research grant.

References

Abdi, J., Vossoughi, M., Mahmoodi, N.M., Alemzadeh, I., 2017, Synthesis of metal-organic framework hybrid nanocomposites based on GO and CNT with high adsorption capacity for dye removal. Chemical Engineering Journal.

Abdullah, H.B., Irmawati, R., Ismail, I., Yusof, N.A., 2020, Utilization of waste engine oil for carbon nanotube aerogel production using floating catalyst chemical vapor deposition. Journal of Cleaner Production, 261, 121188.

AlOmar, M.K., Alsaadi, M.A., Jassam, T.M., Akib, S., Ali Hashim, M., 2017, Novel deep eutectic solvent-functionalized carbon nanotubes adsorbent for mercury removal from water. Journal of Colloid and Interface Science.

Choi, H.-J., Yu, S.-W., 2018, Biosorption of methylene blue from aqueous solution by agricultural bioadsorbent corncob. Environmental Engineering Research, 24(1), 99–106.

Dai, L., Zhu, W., He, L., Tan, F., Zhu, N., Zhou, Q., He, M., Hu, G., 2018, Calcium-rich biochar from crab shell: An unexpected super adsorbent for dye removal. Bioresource Technology.

Duman, O., Özcan, C., Gürkan Polat, T., Tunç, S., 2019, Carbon nanotube-based magnetic and non-magnetic adsorbents for the high-efficiency removal of diquat dibromide herbicide from water: OMWCNT, OMWCNT-Fe_3O_4 and OMWCNT-K-carrageenan-Fe_3O_4 nanocomposites. Environmental Pollution.

Duman, O., Tunç, S., Polat, T. G., Bozoğlan, B. K., 2016, Synthesis of magnetic oxidized multiwalled carbon nanotube-κ-carrageenan-Fe 3 O 4 nanocomposite adsorbent and its application in cationic Methylene Blue dye adsorption. Carbohydrate Polymers, 147, 79–88.

Homayoon, F., Faghihian, H., Torki, F., 2017, Application of a novel magnetic carbon nanotube adsorbent for removal of mercury from aqueous solutions. Environmental Science and Pollution Research.

Hossen, M. Z., Hussain, M. E., Hakim, A., Islam, K., Uddin, M. N., Azad, A. K., 2019, Biodegradation of reactive textile dye Novacron Super Black G by free cells of newly isolated Alcaligenes faecalis AZ26 and Bacillus spp obtained from textile effluents. Heliyon, 5(7), e02068.

Ibrahim, S. M., Badawy, A. A., Essawy, H. A., 2019, Improvement of dyes removal from aqueous solution by Nanosized cobalt ferrite treated with humic acid during coprecipitation. Journal of Nanostructure in Chemistry, 9(4), 281–298.

Jin, Q., Li, Y., Yang, D., Cui, J., 2018, Chitosan-derived three-dimensional porous carbon for fast removal of methylene blue from wastewater. RSC Advances.

Kang, S., Wang Z., Won S., 2020, Adsorption Characteristics of Methylene Blue on PAA-PSBF Adsorbent. Chemical Engineering Transactions, 78, 205–210.

Lellis, B., Fávaro-Polonio, C.Z., Pamphile, J.A., Polonio, J.C., 2019, Effects of textile dyes on health and the environment and bioremediation potential of living organisms. Biotechnology Research and Innovation, 3(2), 275–290.

Maceiras, R., Alfonsín, V., Morales, F.J., 2017, Recycling of waste engine oil for diesel production. Waste Management, 60, 351–356.

Menkiti, M.C., Okoani, A.O., Ejimofor, M.I., 2018, Adsorptive study of coagulation treatment of paint wastewater using novel Brachystegia eurycoma extract. Applied Water Science, 8(6), 1–15.

Price, G. J., Nawaz, M., Yasin, T., Bibi, S., 2018, Sonochemical modification of carbon nanotubes for enhanced nanocomposite performance. Ultrasonics Sonochemistry, 40, 123–130.

Rajabi, M., Mahanpoor, K., & Moradi, O., 2017, Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups: Critical review. RSC Advances.

Plata, D., Hart, J. Reddy C., Gschwend, P., 2009, Early Evaluation of Potential Environmental Impacts of Carbon Nanotube Synthesis by Chemical Vapor Deposition. Environ. Sci. Technol. 2009, 43, 8367–8373

Sa, K., Mahakul, P. C., Subramanyam, B. V. R. S., Raiguru, J., Das, S., Alam, I., Mahanandia, P., 2018, Effect of reduced graphene oxide-carbon nanotubes hybrid nanofillers in mechanical properties of polymer nanocomposites. IOP Conference Series: Materials Science and Engineering, 338, 012055.

Venkatesan, S., Visvalingam, B., Mannathusamy, G., Viswanathan, V., Rao, A.G., 2018, Effect of chemical vapor deposition parameters on the diameter of multi-walled carbon nanotubes. International Nano Letters, 8(4), 297–308.

Wong, S., Ghafar, N. A., Ngadi, N., Razmi, F. A., Inuwa, I. M., Mat, R., Amin, N. A. S., 2020, Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste. Scientific Reports, 10(1), 1–13.

Xiong, W., Zeng, G., Yang, Z., Zhou, Y., Zhang, C., Cheng, M., Liu, Y., Hu, L., Wan, J., Zhou, C., Xu, R., Li, X., 2018, Adsorption of tetracycline antibiotics from aqueous solutions on nanocomposite multi-walled carbon nanotube functionalized MIL-53(Fe) as new adsorbent. Science of The Total Environment, 627, 235–244.

Yaseen, D.A., Scholz, M., 2019, Textile dye wastewater characteristics and constituents of synthetic effluents: A critical review. In International Journal of Environmental Science and Technology (Vol. 16, Issue 2). Springer Berlin Heidelberg.