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Comparison of Drying Method on Acid-functionalized Multi-walled Carbon Nanotube and their Application for Dye Removal

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Abstract. The application of surface modified multi-walled carbon nanotube is one of the emerging adsorbents for removal of pollutants from wastewater, particularly dye pollutants. In this study, the effects of drying methods on acid functionalized MWCNT (f-MWCNT) by using freeze dry or oven dry treatment methods were investigated and compared. It is vital to have a proper drying method in order to attain desired particles sizes and properties. Freeze-dried MWCNT (FD-MWCNT) were more desirable than oven-dried MWCNT (OD-MWCNT), as they were in soft flake form, with no formation of aggregates. Besides, characterization studies were performed to analyze the surface morphology and chemical compositions of the f-MWCNTs. Results revealed that FD-MWCNT has less structural damaged and higher oxygenated functional groups than OD-MWCNT. As for batch dye adsorption experiments, FD-MWCNT has higher performances compared to OD-MWCNT. The maximum dye removal efficiency that FD-MWCNT can achieve was 99% at pH 7, 90 min, 10 mg/L dye initial concentration and 150 rpm. It has been proved that freeze dry treatment is more favorable than oven dry method as the dried MWCNT obtained has superior structure properties and adsorption capability for dye removal.

1. Introduction

Water pollution caused by dyes has gained more attention in recent years [1-3]. Synthetic dyes are widely used in various fields such as textile, pulp, paper, cosmetic, food, plastics, printing industries. Majority of dyes are hard to decolourise due to their complex structure and inert properties. These dyes which are highly toxic and carcinogenic, have triggered a major concern on human health and

living organisms [4, 5]. Therefore, it is essential to treat these dye effluents prior their discharged to the environment.

There are a variety of existing wastewater treatment technologies, which can be categorized intro physical, chemical and biological treatment methods. For instance, coagulation, adsorption, membrane filtration, reverse osmosis, photocatalytic, oxidation, and solvent extraction [5-8]. Among all the existing technologies, adsorption technique is recognized as one of the most effective treatment method due to its low cost, simplicity, efficiency and environmental friendly [9]. The most commonly used adsorbents are kaolinite, natural clay, fly ash, zeolite, and activated carbon [10-13].

Recently, carbon nanotube (CNT) has received immense attention by researchers as promising adsorbents for removal of wastewater treatment [14-16]. CNTs are known for their unique physiochemical properties, such as large specific surface area, superior chemical, mechanical and thermal properties [17, 18]. Surface modification of CNT is essential to enhance its dispersibility and solubility, as well as to remove its surface impurities [19, 20]. There are various functionalization methods, such as acid oxidation treatment, coating with surfactant and polymer, as well as impregnation with metal or metal oxides [21, 22]. One of the most commonly used surface modification method is via acid functionalization due to its ease of preparation and cost-effective [23, 24]. Generally, strong oxidizing agents used for acid treatment of MWCNTs are nitric acid, sulphuric acid, hydrochloric acid and potassium permanganate [25].

However, one of the problems occurred during acid functionalization of MWCNTs is the disruption on the graphitic structure and shortening length of MWCNTs. The most commonly used drying methods for powder formed materials are oven dried and freeze dried methods. According to Turgunov and Hyo Noh [26], the operational condition of drying process can exert significant influence on the surface structures and functionalities of f-MWNCTs. Thus, the drying process of the MWCNTs after acid treatment must be taken with care.

Despite of the numerous studies in the field of MWCNT acid functionalization, there is a lack of in-depth studies on selection of most appropriate drying methods of MWCNTs after acid treatment in order to obtain desired f-MWCNTs powders. Therefore, the primary objective of this study is to perform a comparative study on the drying method of f-MWCNTs using oven dried or freeze dried treatment methods. Besides, characterization studies, such as Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX), were carried out to investigate the surface morphology and chemical compositions of both freeze dried and oven dried f-MWCNTs. Lastly, the performances evaluation of the dye removal efficiency of both f-MWCNTs were also investigated and compared.

2. Materials and Methods

2.1. Materials

98% purity MWCNTs with diameter ranging from 16 – 23 nm obtained from previous study [24], 65% nitric acid (HNO_3), 95% sulphuric acid (H_2SO_4), hydrophilized polytetrafluorethylene (PTFE) filter with pore size of 0.45 μm and diameter of 47 mm, Methylene Blue (MB). All the chemicals were purchased from Sigma Aldrich and were used as received.

2.2. Sample preparation and functionalization of MWCNTs

Acid functionalization of MWCNTs were performed according to the literature reported by Buang, et al. [27]. Firstly, 0.3 g of raw MWCNTs was dispersed in the mixture of concentrated HNO_3 and H_2SO_4 acid (1:3 v/v ratio) under 2 hours ultrasonication at 40ºC. The mixture was then filtered through PTFE membrane under vacuum. The filter cake was washed with distilled water thoroughly until pH 7. Finally, the samples were dried in an oven or freeze dryer. The OD-MWCNT was dried in the oven for 8 hours at 100ºC. On the other hand, the FD-MWCNT was frozen in refrigerator at 4ºC and then put in a freeze dryer at -50ºC and 0.133 bar or 24 hours. Both dried f-MWCNTs powders were kept in duran bottles until further analyses.

2.3. Characterization studies

The structure and morphology of pristine and f-MWCNTs were analyzed by Field Emission Scanning Electron Microscope (FEI Quanta 400 SEM) coupled with Energy dispersive X-ray analysis (EDX). The quantitative elemental analysis of the MWCNTs were investigated by EDX. Moreover, the concentration of the residual MB solutions were analysed by using UV-vis spectrophotometer (Lambda 25 UV/Vis Double Beam, Perkin Elmer).

2.4. Adsorption experiments

60 mg/L MB stock solution were prepared. The stock solution was then diluted to the required concentrations. The batch adsorption experiments were conducted by preparing 50 ml of diluted MB solutions with different concentrations in each labelled beaker. The effect of process parameters, such as pH, contact time, initial dye concentration and agitation speed for analysed using single factor optimization. The pH of the solutions were prepared to their desired pH values by adding 0.1 M HCl and 0.1 M NaOH gradually. 20 mg of f-MWCNTs were then added into each beakers and agitated at 150 rpm, at room temperature for 60 min. Lastly, the samples were filtered and the residual concentration of the MB was analyzed by using UV-vis spectrophotometer at a maximum wavelength of 665 nm. Fig. 1 shows the 60 mg/L of MB stock solution and its chemical structure.

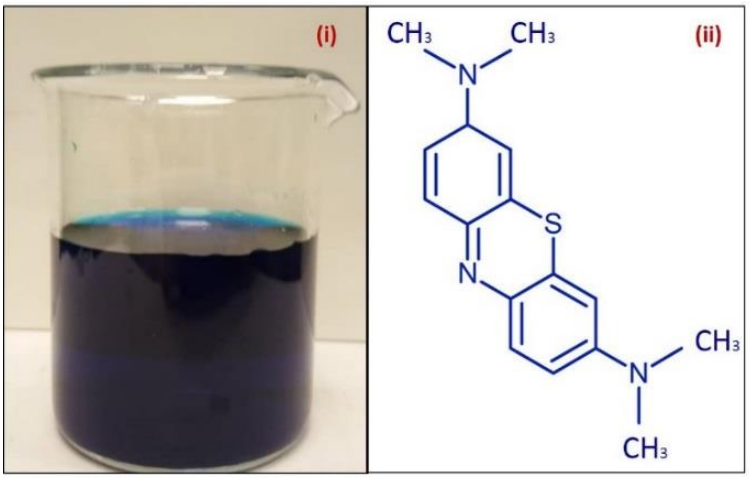

Figure 1: (i) Stock solution of MB and (ii) its chemical structure

The dye removal efficiency of the f-MWCNTs was calculated by using Eq. (1) below:

$$E(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final MB concentrations.

3. Result and Discussion

Fig. 2 displayed both OD-MWCNTs and FD-MWCNTs. It was observed that the texture of OD-MWCNT was hard and rigid. They tend to form aggregates, which makes them difficult to dissolve in solvents. On the other hand, the FD-MWCNT sample obtained was in soft and powder form.

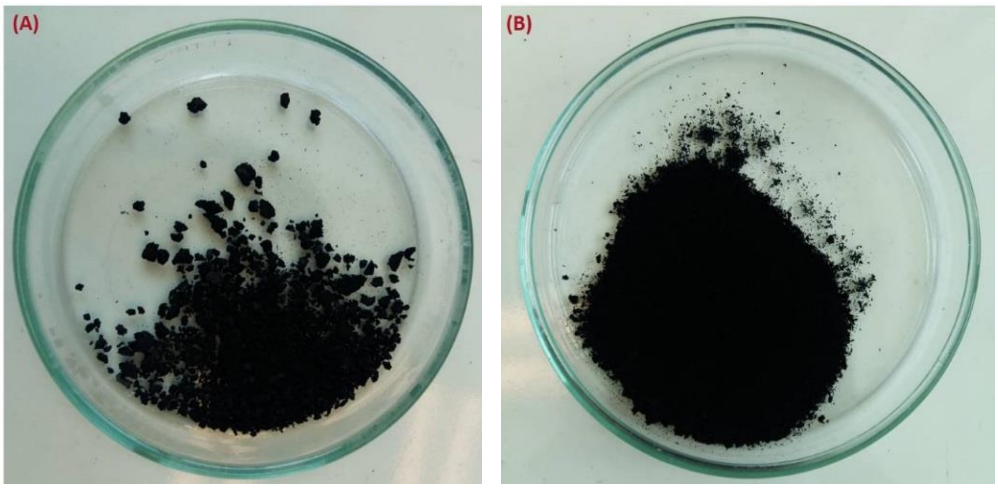

Figure 2. A) OD-f-MWCNTs (B) FD-f-MWCNTs.

3.1. SEM surface morphology

The structural and surface morphology of MWCNTs samples were evaluated by using SEM. Fig. 3 displayed the SEM images of pristine MWCNTs and both f-MWCNTs with the magnification scale of 500 nm. It shows that the pristine MWCNT has a smooth surface with bundles of tangled tubes. However, it is clear from Fig. 3(i) that pristine MWCNT contain many impurities on its surface. On the other hand, both OD-MWCNT and FD-MWCNT have rougher surface structures due to the attachment of oxygenated functional groups on their surface after acid treatment. There were no obvious presence of impurities trace in both f-MWCNTs due to the oxidation during the acid treatment. SEM observation showed that FD-MWCNTs has less structural damage on its surface. From Fig.3 (ii), it is clear that the surface of OD-MWCNTs was shortened and more layered. The alteration of surface structure of OD-MWCNT was due to the exposed of high temperature treatment for long times [28]. A similar result trend was obtained by Turgunov and Hyo Noh [26].

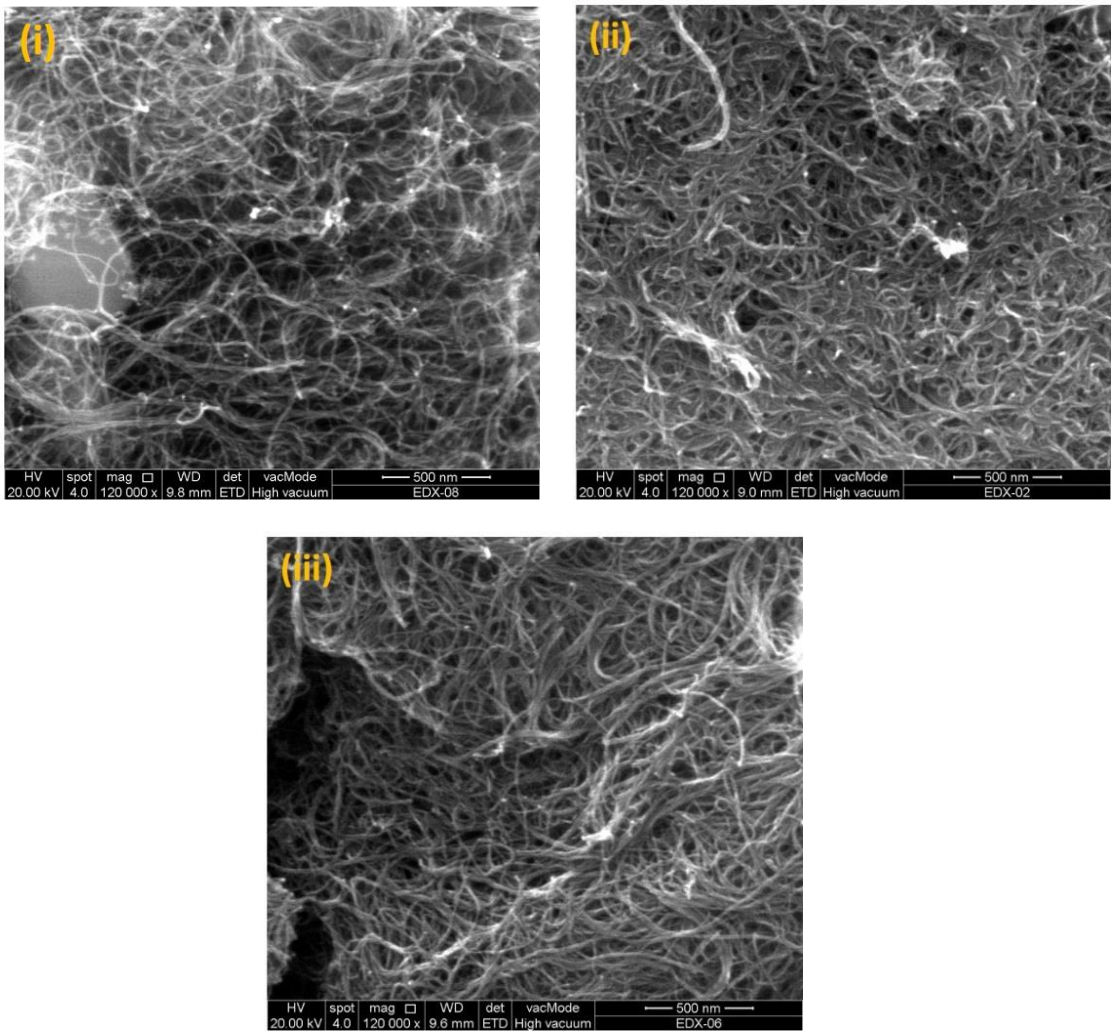

Figure 3. SEM images of MWCNTs samples with scale bar of 500 nm: (i) pristine MWCNTs, (ii) OD-f-MWCNTs and (iii) FD-f-MWCNTs.

3.2. EDX Analysis

The chemical compositions present in the pristine MWCNT, OD-MWCNT and FD-MWCNT were determined by using EDX. Results revealed that pristine MWCNT have some presence of inorganic and metal impurities, such as calcium (Ca), phosphate (P), magnesium (Mg), potassium (K) and iron (Fe). After acid functionalization, these metal impurities were removed from the MWCNTs. Besides, f-MWCNTs exhibited higher intensity of oxygen content due to generation of oxygenated functional groups after acid treatment. Moreover, results also proved that FD-MWCNT can obtain MWCNTs with higher oxygenated functional groups than OD-MWCNT. Similar results had been reported by [26, 29]. Table 1 illustrated the results for chemical compositions of the samples extracted from EDX analysis.

Table 1. Chemical composition of pristine MWCNT, OD-MWCNT and FD-MWCNT

Elements	Chemical composition in Weight (%)		
	Pristine MWCNT	**OD-MWCNT**	**FD-MWCNT**
C	90.21	74.46	46.18
O	8.21	18.73	31.99
Na	0.29	0.18	0.28
Al	0.28	2.82	1.85
S	0.16	3.80	19.7
Ca	0.38	-	-
P	0.24	-	-
Mg	0.07	-	-
K	0.07	-	-
Fe	0.08	-	-

3.3. Performance evaluations on dye adsorption

3.3.1 Effect of pH

The pH of the solution is one of the key influencing factors for the adsorption of MB onto the f-MWCNTs. The pH of the solution can affect the surface charge of the adsorbent, degree of ionization of dyes, and the structure of the dye molecule. The effect of pH on the removal of MB using OD-MWCNT and FD-MWCNT was illustrated in Fig. 4. The optimum pH for MB removal using OD-MWCNT and FD-MWCNT were observed at pH 7. The dye removal efficiency of both f-MWCNTs increase from pH 2 to pH 7. The higher the pH value, the lower the H^+ ions, resulting in more favorable dye removal process. However, the further increase of pH, lead to decrease in dye removal efficiency. This is due to the decrease of surface charge, leading to a reduction in the electrostatic repulsion between the surface charge of MB and f-MWCNTs [30].

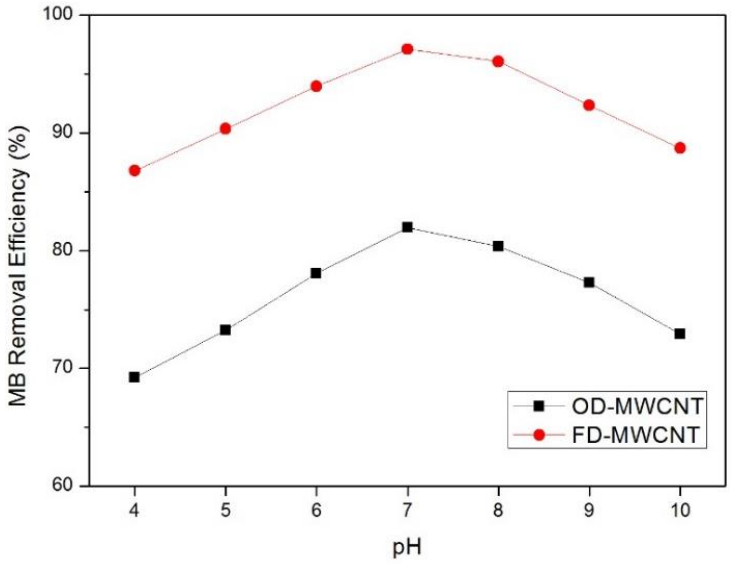

Figure 4. Effect of pH on MB removal efficiency using OD-MWCNT & FD-MWCNT.

3.3.2 Effect of contact time and initial concentration of MB

The effect of contact time and initial concentration of MB on adsorption process were investigated to determine the efficiency of the adsorbents as well as the equilibrium time. The batch adsorption experiments were carried out at constant operating conditions of pH 7, room temperature and 150 rpm agitation speed. The result of the effect of the contact time and initial MB concentrations on the MB removal efficiency using OD-MWCNT and FD-MWCNT were presented in Figure 5.

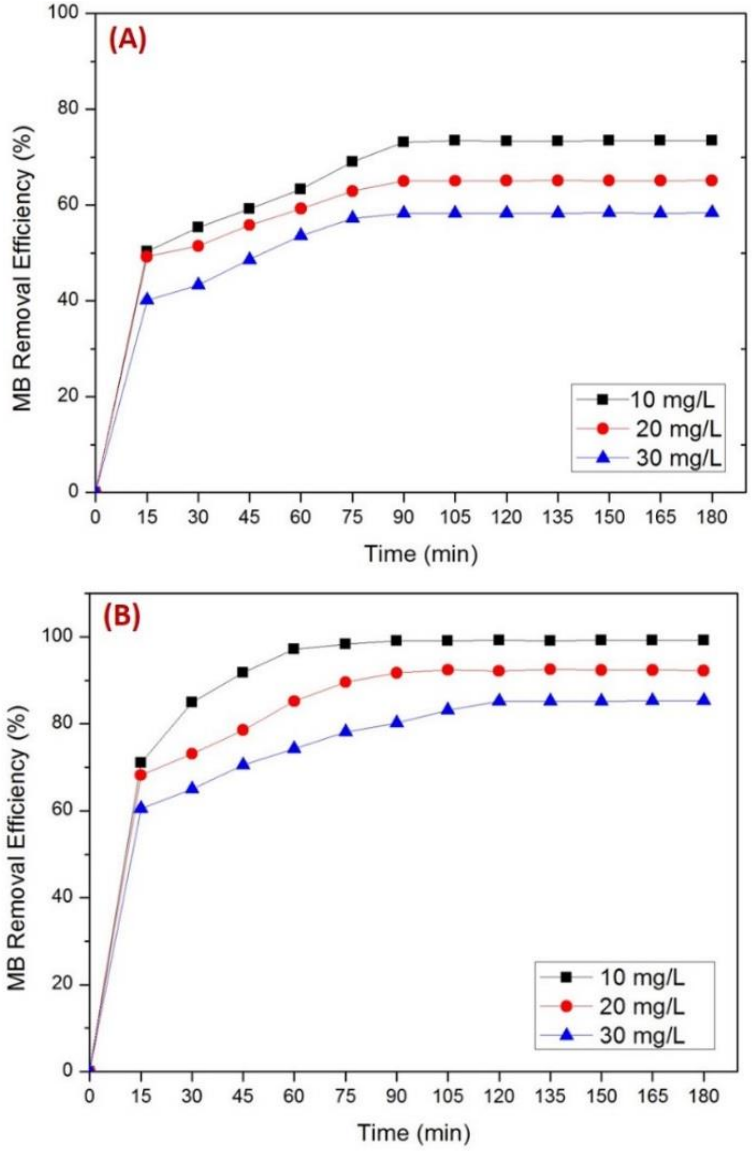

Figure 5. Effect of contact time on the removal efficiency of (A) OD-MWCNT (B) FD-MWNCT at different initial MB concentrations.

Notably, the dye adsorption efficiency of both f-MWCNTs decreases with increasing initial dye concentrations. This is due to the saturation of the adsorption sites on the surface of the adsorbents. The dye removal efficiency of both f-MWCNTs increases rapidly within the first 15 min, and increase gradually up to 90 min. The fast uptake of dye removal capability at initial stage were due to the large number of vacant adsorption sites on the adsorbent surface. After 90 min, as there were no significant changes in the adsorption rate up to 180 min as equilibrium states were attained. The decreased

adsorption rates were due to the lack of available active sites due to the formation of MB monolayer on the adsorbent surfaces. At 10 mg/L initial dye concentration, FD-MWCNTs can achieve higher MB dye removal efficiency up to 99% dye removal efficiency within 90 min. On the other hand, there was only 75% dye removal takes place for OD-MWCNT at similar operating conditions. This might due to the lower surface area of OD-MWCNTs due to the formation of aggregation and rigid particles after oven dried. The result was in good agreement with previous researchers [31].

3.3.3 Effect of agitation speed

The effect of agitation speeds on MB removal was studied by varying the speed from 50 rpm to 150 rpm, while keeping all other parameters constant. The maximum dye removal efficiencies achieved by both OD-MWCNT and FD-MWCNT were at 150 rpm. It demonstrated that the higher the agitation speed, the higher the removal efficiency of MB for both f-MWCNTs. This is due to the increase in collision frequency and the interaction between surface functional groups on the f-MWCNTs and the MB ions [32]. Similar findings were observed in the previous studies [33, 34].

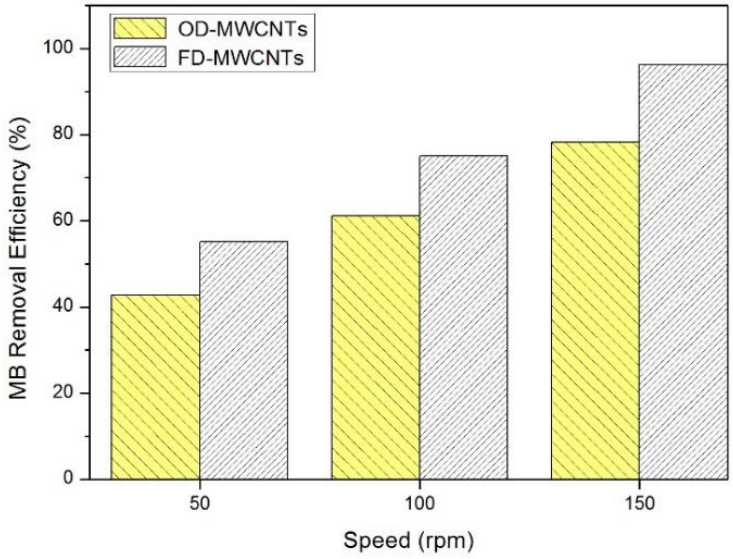

Figure 6. Effect of agitation speed on adsorption of MB.

Table 2 summarized the advantages and disadvantages of drying f-MWCNTs using oven-dried and freeze-dried treatment methods.

Table 2. Advantages and disadvantages of oven-dried and freeze-dried treatment methods.

Oven drying method	Freeze drying method
✓ Shorter drying time	✓ Soft and powder form
	✓ Better dispersibility
	✓ Higher oxygenated functional groups
× Compact and hard texture	× Time consuming for drying period
× Formation of agglomeration	
× Poor dispersibility in solvent	

4. Conclusion

In conclusion, vacuum freeze dried treatment method is more preferable than oven dried method for drying of f-MWCNTs. As compared OD-MWCNT, FD-MWCNT has more desirable properties and less surface structural damage. It was found that the adsorption efficiencies of f-MWCNTs were dependent on the effect of pH, contact time, initial dye concentrations and agitation speed. Results showed that FD-MWCNTs can achieve better MB adsorption ability than OD-MWCNTs. It can take up to 99% of MB within 90 minutes at its optimum conditions of pH 7, 90 min contact time, 10 mg/L initial dye concentration and 150 rpm agitation speed. Thus, OD-MWCNT is proven to be a promising adsorbent for removal of dyes from wastewater.

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