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Statistical Evaluation of the Production of Urea Fertilizer-Multiwalled Carbon Nanotubes using Plackett Burman Experimental Design

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Abstract

Plant growth rate is significantly dependent on application of nitrogenous fertilizer which mainly contributed by urea fertilizer (UF). Nanotechnology advancements in nutrition strategies for plants have attempted to assist plant nutrition for efficient plant growth. The development of carbon nanomaterials (NMs) including Multi-walled carbon nanotubes (MWNTs) in conjunction with the advancement in biotechnology has expanded their application area of in the field of agriculture. The aim of the work is to identify the significant process parameters to attach urea fertilizer (UF) onto MWNTs. The UF-MWNTs was than characterized optically and chemically to confirm their bonding. Comparison study was also conducted between UF-MWNTs and UF-functionalized MWNTs on total N content bonding to the MWNTs. The surface functional groups produced from functionalization process are essential for further modification of MWNTs and facilitate the separation of nanotube bundles into individual tubes. Optical, vibrational spectroscopy and chemical characterization were conducted on the samples using TEM, FT-IR and total N analysis confirmed the successful bonding of urea onto MWNTs. Plackett-Burman Experimental Design showed, two out of nine investigated parameters (amount of functionalized MWNTs and percentage of functionalization) were found significant in producing successful attachment of UF onto functionalized MWNTs (fMWNTs).

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Keywords: Urea Fertilizer, Multiwalled Carbon Nanotubes, Functionalization, Nitrogen Content, Growth Rate.

1. Introduction

Nanotechnology advancements in nutrition strategies for plants attempt to solve Nitrogen (N) losses via fertilizer application by introducing Multi-wall carbon nanotubes (MWNTs) as a carrier to improve nutrient uptake by plant

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cells (Torney et al., 2007; Gonzales-Melendi et al., 2008; Serag et al., 2011). Upon successful delivery into the cells, the absorption and utilization of N by the plant can be increased leading to enhanced plant growth. However, production of MWNTs to suit this purpose has to be optimized. Many process parameters have been identified to be important for the production suitable UF-MWNTs fertilizer complex. One of the parameter is functionalization of MWNTs. Functionalization of MWNTs have many advantages: it can overcome the toxicity of MWNTs and this is important to eliminate cross contamination in the food chain during crops agricultural activity. Sayes et al. (2006) reported a high degree of CNTs functionalization would lead to a significant reduction in toxic effects. Furthermore, functionalization is important for further modification of MWNTs. Thus, functionalization on MWNTs is essential in order to use them in agriculture field. The main aim of this work is to use Plackett-Burman design of experiment to screen the most important parameters for sproducing UF-MWNTs, by determining total N as the respond. Upon successful bonding between both, the product was analyzed physically and chemically.

2. Literature Review And Hypotheses

- *Nitrogeneous Fertilizer*

Nitrogenous fertilizer is vital for efficient paddy growth. Referring to the International Fertilizer Industry Association's (IFA) Fertilizer Outlook 2013-2017, global nitrogen (N) fertilizer demand would grow slightly to 107.5 million metric tons of N. Urea fertilizer (UF) is a main source of N fertilizer, since it contain high amount of N (46%). However, it was reported that between 50 and 70% of the nitrogenous fertilizer is lost through leaching and gas emission of ammonia and nitrogen oxides to the atmosphere (Maene, 1995). These may contribute to unfavourable environmental impact and higher operational cost to farmers. Uncontrolled applications of UF also have adverse effect to aquatic life due to eutrophication causing excessive algae growth and decreasing level in water bodies.

- *Nanomaterials Delivery System*

Nanotechnology uses NMs having one or more measurements in the range of 100 nm or less (Auffan et al., 2009). Others refer to NMs as engineered NMs (ENMs) measuring <100 nm in at least one dimension and specifically engineered for an application. Generally, their key advantages include size-dependent qualities and a high surface-to-volume ratio (Miralles et al., 2012).The NMs delivery system is targeting the plant to take up nutrients efficiently and enhance the germination rate of plants by improving the intake of water as well as oxygen (Zheng et al., 2005 and Khot et al., 2012). Hence, leaching and losses of nutrients to unintended targets like soil are reduced.

In agriculture, research on smart delivery systems reported on the delivery of pesticides encapsulated in NMs for UV-shielding (Li et al., 2007) and assisted delivery of genetic material for crop improvement (Vijayakumar et al., 2010). Ghormade et al. (2011) and Wilson et al. (2008) have shown potential applications of NMs in agriculture to reduce the use of fertilizers by assisting in the controlled-and slow-release of fertilizer. The NMs smart delivery system has led to the advancement of agriculture technology due to unique properties such as time control, specific targets, and multifunctional characteristics avoiding biological barriers for effective targeting (Nair et al., 2010). In addition, the application of NMs reduces fertilizer use and increases agriculture yields through an optimized nutrient management (Srilatha, 2011; Sharon et al., 2010; Bhattacharyya et al., 2010; Perez-de-Luque and Rubiales, 2009; Garcia et al., 2010; Rashidi and Khosravi-Darani, 2011).

The developments of carbon NMs in conjunction with the advancement in biotechnology have expanded the application area of carbon NMs in the field of agriculture. Application of carbon NMs holds great promise for progress in the agricultural activity (Ghodake et al., 2010; Khodakovskaya et al., 2013; Canas et al., 2008). The most studied carbon based NMs are the single wall carbon nanotubes (SWCNTs), multi wall carbon nanotubes (MWCNTs), nano graphite colossal carbon (CC) and fullerol. Carbon NMs with special physicochemical properties were reported to have a unique ability as molecular transporter for walled plant cells (Liu et al., 2009), which stimulates crop growth, improves the soil environment and promotes crop growth metabolism (Lu et al., 2002; Xiao et al., 2008; Liu et al., 2007) . We examined the combination of MWNTs with UF to develop UF-MWNTs fertilizer and analyses the morphology of the samples as well as the chemical interaction occurred between them.

- *Plackett-Burman Experimental Design*

Developing a UF-MWNTS fertilizer involved a lot of evaluated parameters that affect the total amount of N contain in the fertilizer. The Plackett–Burman experimental design is useful for screening of significant parameters from a large number of process variables.

3. Methodology

3.1. Research Goal

The aim of this study is to screen significant variables that affect the development of UF-MWNTs fertilizer process by using Plackett Burman experimental design of experiment. Analyses were conducted using statistical software Design Expert. The identified factors were amount of MWNTs, percentage of functionalization, stirring time, stirring temperature, agitation, sonication frequency, sonication temperature, sonication time and amount of ammonium chloride with corresponding response Total N attached on the surface of MWNTs.

3.2. Preparation of UF-MWNTs fertilizer

Commercially available chemical vapour deposition grown MWNTs with purity >95% were used. FMWNTs with 4 wt% of functional groups were purchased from Cahaya Tech, Malaysia. Various amounts of MWNTs and fMWNTs were sonicated before stir with urea fertilizer at various time, temperature and agitation. Samples were then dried in oven at 70°C for 280 minutes.

3.3 Characterization

Fourier transform-IR spectra used to confirm the functional groups of UF-MWNTs fertilizer, obtained on a Jasco FTiR-6100 with attenuated total reflectance (ATR) method. Each sample was scanned with resolution, 4cm-1 within the range 400-4000 cm-1 to obtain the spectrum. A transmission electron microscope (H-7600, 120 kV, Hitachi) was used to observe the morphology of the MWNT and functionalized MWNTs before and after their reaction with UF.

3.5 Statistical Analysis of the data from the Plackett-Burman design

Plackett-Burman design of experiment was used to screen of the significant parameters with respect to their main effects and not the interaction effects between various parameters constituents (Plackett and Burman, 1944). The experimental design using Plackett–Burman design of experiment was produced using +1 and -1 for each variable as in Table 1 where twelve experiments have been conducted. Amara et al. (2014) reported that the main effect of both of +1 and -1 for each variable has been calculated from the following formula:

$$\text{Main effect} = \sum(+1)/n_{(+1)} - \sum(-1)/n_{(-1)} \quad (1)$$

In the case of UF-MWNTs fertilizer, the values that appear upper to the x-axis in the main graphs as in Figure 1 have positive effects on the UF-MWNTs fertilizer, while those that appear under the x-axis have negative effects on the UF-MWNTs. The variables whose confidence levels % were ≥ 90% were considered to significantly affect the UF-MWNTs. Variables with confidence level% less than 90% till 70% were considered as being effective (Stowe and Mayer, 1966).

Table 1. Plackett-Burman Experimental design.

Run	MWNTs (wt%)	Functionalization (%)	stirring time (h)	stirring temp (˚C)	Agitation (rpm)	frequency (Hz)	sonic temp (˚C)	sonic time (min)	NH_4Cl (mg)	Total N (%)
1	0.6	4	6	65	250	high	0	5	0	1.4
2	0.1	0	6	65	50	high	40	5	4	0.46
3	0.6	0	18	65	250	low	0	5	4	0.24
4	0.1	0	6	25	50	low	0	5	0	0.3
5	0.1	4	6	65	250	low	40	30	4	1.41
6	0.6	4	6	25	50	high	0	30	4	1.89
7	0.1	4	18	65	50	low	0	30	0	1.27
8	0.1	4	18	25	250	high	40	5	0	1.63
9	0.6	0	18	65	50	high	40	30	0	0.36
10	0.1	0	18	25	250	high	0	30	4	0.36
11	0.6	0	6	25	250	low	40	30	0	0.28
12	0.6	4	18	25	50	low	40	5	4	1.8

4. Results and Discussion

4.1 Screening of significant variables using Plackett Burman design

A total of nine variables were analyzed with regard to their effects on Total N analysis on UF-MWNTs fertilizer using a Plackett–Burman design (Table 1). The components were screened at the confidence level of 95% and 70-95%. Rafaat et al. (2012) reported that if the components showed significance at or above 95% confidence level, but the main effect is negative, it indicated that the component was effective in total N production on the surface of MWNTs but the amount required was lower than the lower value (-1) in Plackett-Burman design of experiment. However, if the main effect is positive, higher value of the parameters from the high (1) value was needed during further optimization studies.

Referring to the Main effect on Total N graph in Figure 1, functionalization shows the most significant factor that give positive effects for Total N bonding on the surface of MWNTs. The other parameters that give positive main effect value were amount of MWNTs, frequency of sonication, sonication temperature and amount of ammonium chloride. Among these parameters that give positive main effect value, amount of MWNTs, frequency of sonication and amount of ammonium chloride give confidence level at 70-95%. Hence, they should be applied at higher than (+1) value during further optimization step. While parameters which give negative main effect value (stirring temperature, agitation and sonication time) but with high confidence level (>90%) should be applied at lower value.

The adequacy of the model was calculated, and the variables evidencing statistically significant effects were screened via Student's t-test for ANOVA (Table 2). Factors evidencing P-values of less than 0.05 were considered to have significant effects on the response, and were therefore selected for further optimization studies. Functionalization with probability value of 0.0008 and confidence level 99.92%, was determined to be the most significant factor, followed by stirring temperature (0.033) with confidence level 96.7%. The lower probability values indicate the more significant factors affecting the nitrogen content binding onto the surface of MWNTs. However, stirring temperature exerted a negative effect, functionalization and amount of MWNTs, exerted positive effects on Total N content. Thus, both main effect analysis and ANOVA reveal functionalization and amount of MWNTs was included as the effective Total N production in UF-MWNTs fertilizer and selected to be further optimized. Amount of ammonium chloride as filler was kept at higher value. All other insignificant variables were used at lower value.

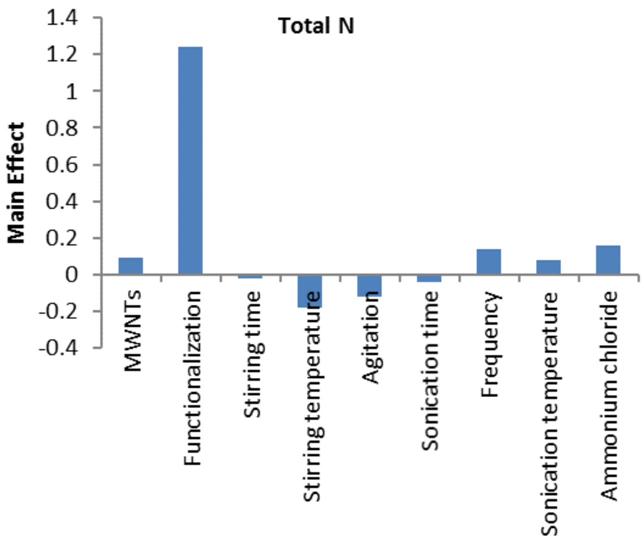

Fig. 1 Main effect on Total N.

Table 2: Estimated Effect, Standard Error, Corresponding F and P Values and Confidence Level For Total N Content In Nine Variables Plackett–Burman Design Experiment.

Parameter	Estimate	Standard Error	F-value	p-value	Confidence level %
MWNTs	0.045	0.017400511	6.688	0.1226	87.74
Functionalization	0.617	0.017400511	1255.96	0.0008	99.92
Stirring time	-0.007	0.017400511	0.147	0.7385	26.15
Stirring temperature	-0.093	0.017400511	28.771	0.033	96.7
Agitation	-0.063	0.017400511	13.248	0.0679	93.21
Sonication time	0.067	0.017400511	14.679	0.0619	93.81
Frequency	0.04	0.017400511	5.284	0.1483	85.17
Sonication temperature	-0.022	0.017400511	1.55	0.3392	66.08
Ammonium chloride	0.077	0.017400511	19.413	0.0478	95.22

4.2 Fourier Transform Infrared Spectroscopy (FTiR).

FTiR aims to study spectral changes in position or shape occurred in the distribution of frequencies which use to identify the presence of functional group (Queiroz et al., 2003 and Yu et al., 2004). Figure 2 shows the FTiR spectra of fMWNTs, UF-MWNTs with 0.6wt% of fMWNTs (FMU 1), UF-MWNTs with 0.1wt% of functionalized MWNTs (FMU 2), and UF-MWNTs with 0.6wt% of MWNTs (MU). The outer walls of MWNTs are chemically inactive. Functionalization process will activate the sidewalls. Chemical functionalization is based on the production of covalent bond between the functional groups with the carbon of MWNTs (Jeon et al., 2011). It can be performed at the end caps of nanotubes or at their sidewalls which may have many defects. Hence, upon reactions between urea and fMWNTs, it is strongly suggested that covalent bondings occurred between NH_2 groups of UF and carboxyl groups of fMWNTs.

The spectra mainly characterized by bands at 3300-2500 (O-H stretching vibration), 1700-1725 cm^{-1} (C=O stretching vibration) and 1210-1320 cm^{-1} (C-O stretching vibration) correspond to the vibration of the carboxylic acid groups (Wei et al., 2010). In the IR spectra of UF-MWNTs, the bands around 1640-1690 cm^{-1}, 1510-1600 cm^{-1}, 1376-1388 cm^{-1} and 1120-1290 cm^{-1} could be assigned to C=O stretching vibration, N-H bending, CH_2 bending and C-N stretching. These characteristic spectral are attributed to amide (Wei et al., 2010).

Any changes in peak position or shape reveal a change has happened in the distribution of frequencies included in that particular vibration mode. By comparing the FTiR spectra of fMWNTs and UF-MWNTs, it could be seen that the transmission peak of O-H stretching vibration at 3018 in the IR spectrum of fMWNTs (Figure 2 (A)) disappeared in the IR spectrum of UF-MWNTs [Figure 2 (B and C)], indicating that the O-H groups in fMWNTs might react with the amino groups in the urea fertilizer during the functionalization process. Also, C=O (1739 cm^{-1}) and C-O (1219 cm^{-1}) stretching vibration attributed to fMWNTs were observed replaced with new shape of transmission peak that appears, corresponding to N-H bending and C-N stretching vibration at 1519 and 1219 cm^{-1} respectively after fMWNTs was further functionalized with UF. The NH_2 groups from UF can react with the carboxyl groups (COOH) on the surface of fMWNTs and produce amide groups (Gao et al., 2005). Thus the results from the FTiR spectra confirm that chemical functionalization has occurred between fMWNTs and UF instead of physical functionalization (non covalent) only.

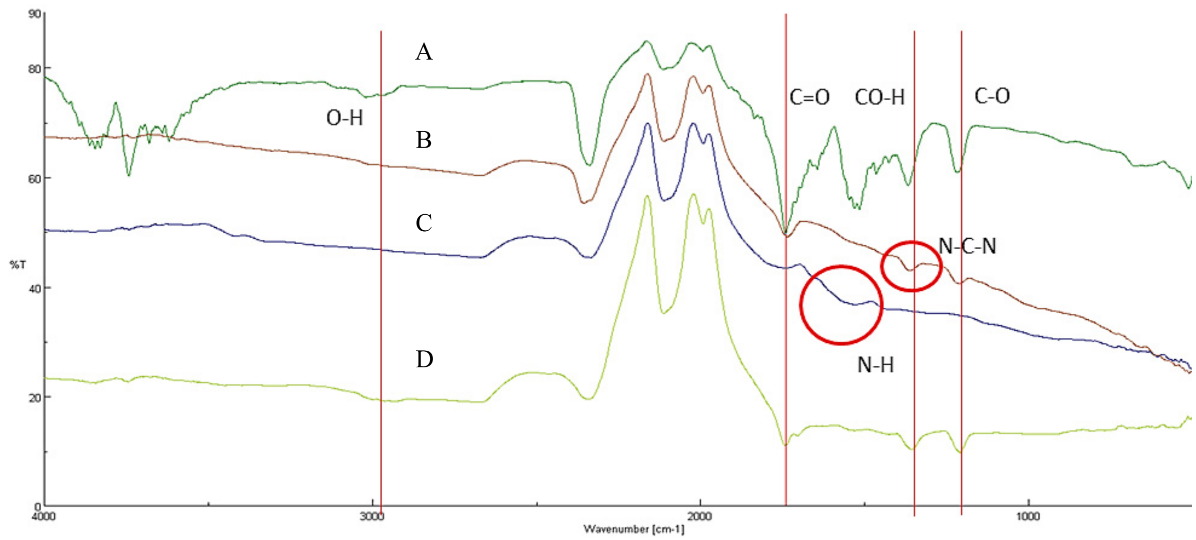

Fig. 2. FTiR spectra of (A) fMWNTs, (B) UF-fMWNTs with 0.6 wt% fMWCNTs, (C) UF-fMWNTs with 0.1 wt% fMWCNTs and (D) UF-MWNTs.

4.3 Transmission Electron Microscopy (TEM)

Figure 4 shows the TEM images of MWNTs, fMWNTs, UF-fMWNTs and UF-MWNTs. The morphology of MWNTs (Figure 4a) is clearly shown. The MWNTs have multiwall along the tubular structure with hollow structure at the centre. Compared with fMWNTs (Figure b), even the hollow and tubular structure are still retained, but a few multiwall structure have broken and open. Functionalization process was found to cause defects to the sidewall while most of the sidewall still preserves their basic multiwall structure. These defects are important to MWNTs intended for further modification. Figure 4c shows the MWNTs after interaction with UF. It is clearly observed that MWNTs are still in the multiwall tubular structure which implies only physical interaction occurs between them. However, further modification of fMWNTs with UF (Figure 4d) reveal most of the tubular multiwall structure have been ruptured as a result of chemical interactions. These TEM results are in agreement with FTiR spectra that demonstrated chemical reaction occurred between UF and fMWNTs, discussed earlier. Hence, functionalization leads to significant further modification of MWNTs with UF.

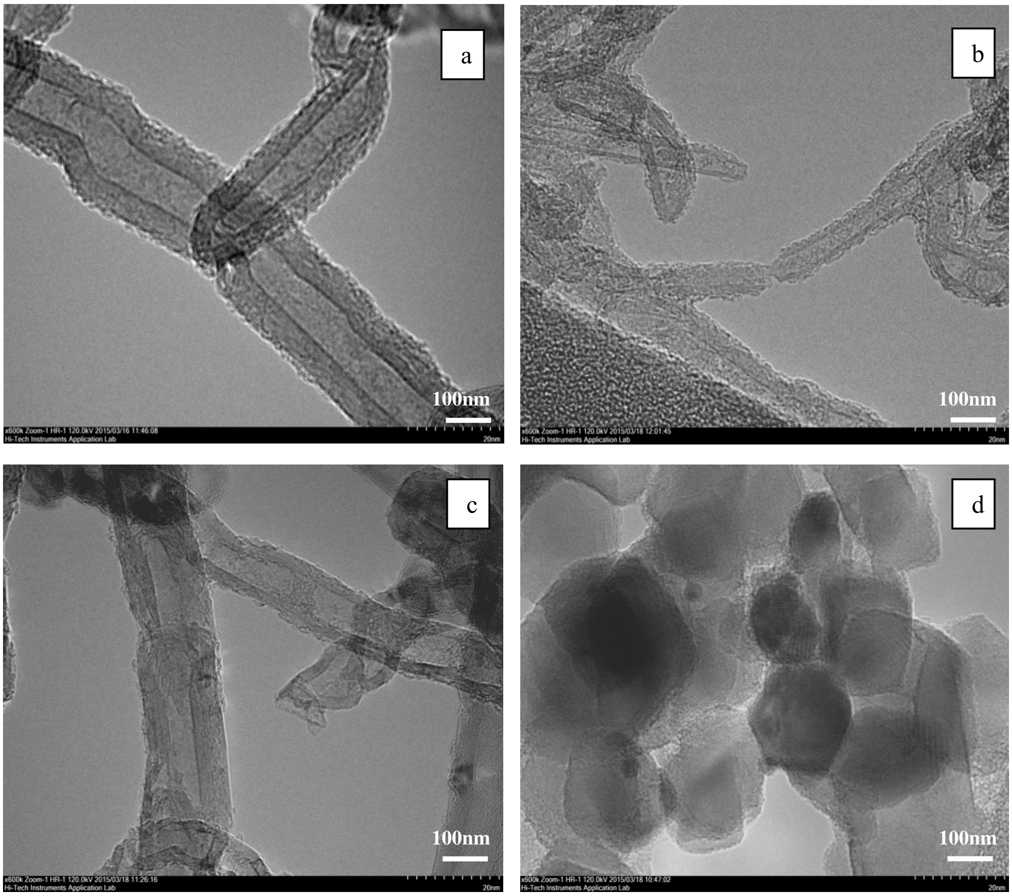

Fig. 3. TEM micrographs of the (a) MWNTs, (b) fMWNTs, (c) UF-MWNTs and (d) UF-fMWNTs.

5. Conclusion

In conclusion, Plackett Burman design and analysis is effective for statistically screening of significant parameters from a large number of process variables. Functionalization and amount of MWNTs used were the most significant factors that affect Total N content in UF-MWNTs fertilizer. As reveal by FTiR spectra and TEM micrographs, MWNTs only implies physical reaction with UF, while fMWNTs shows significant chemical reaction with UF. The results suggest the importance of functionalization and amount of MWNTs for further optimization step in developing novel urea-MWNTs fertilizer for plant growth.

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