



Characterization of Carbon Nanotubes Loaded with Nitrogen, Phosphorus and Potassium Fertilizers

Mohammed Nagib Abdel-Ghany Hasaneen, Heba Mahmoud Mohammad Abdel-Aziz*, Aya Moheb Omer

Department of Botany, Faculty of Science, Mansoura University, Mansoura, Egypt

Email address:

hebamabdelaziz@mans.edu.eg (H. M. M. Abdel-Aziz)

*Corresponding author

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Abstract: Carbon nanotubes either single-walled or multiwalled have been a focus in materials research. Carbon nanotubes are tubular structures of nanometer diameter and large length/diameter ratio. The nanotubes may consist of one, tens and hundreds of concentric shells of carbons with adjacent shells separation of ~0.34 nm and they can have different individual structures, morphologies and properties. Hence, a wide variety of synthetic methods have been developed to produce the desired materials and properties for scientific studies or technological applications. In this study we succeeded to develop a chemical synthetic method that allows us to prepare carbon nanotubes (CNTs) from graphite powder easily and inexpensively at low temperatures (below 70°C) and without applying pressure.

Keywords: Carbon Nanotubes, Fertilizer, Synthesis, Zeta Potentials, Infra-red Spectroscopy

1. Introduction

Carbon nanotubes (CNTs) are tubular structures that are typically of nanometer diameter and many micrometres in length, consist of a single layered cylinder which known as single walled carbon nanotubes (SWCNTs); or it may contain multiple concentric shells of carbons with adjacent shells separation of 0.34 nm and large length/diameter ratio which known as multi-walled carbon nanotubes (MWCNTs) [1]. Diameters of SWCNTs are typically between 0.8 to 2 nm and MWCNTs are 5 to 30 nm, although MWCNTs diameters can exceed 100 nm. This fascinating new class of materials was first observed by Endo [2], and later by Iijima [3] in the soot produced in the arc-discharge synthesis of fullerenes.

Carbon nanotubes (CNTs) are used in many fields such as optics, mechanics, electronics and biology. Carbon nanotubes (CNTs) have three shapes; chiral, zigzag, or armchair. Single walled carbon nanotubes may be in all three forms, while multiwalled CNTs exhibit only the armchair or zigzag.

The methods for the synthesis of CNTs can be divided into three types: laser ablation method, arc discharge and chemical vapor deposition method (CVD) [4]. The Chemical

Vapor Deposition (CVD) is the most appropriate method for synthesizing of CNTs with controlled diameter, length and number of walls [5]. It involves the decomposition of a gaseous or volatile compound of carbon, catalyzed by metallic nanoparticles [6]; both MWNT and SWNT synthesis have been well developed using CVD. However, the process of carbon nanotubes synthesis remains cost and difficult as the high temperatures and pressures are required.

CNTs can act as a nutrient carriers as in nanofertilizers which their dimensions ranging from 30 to 40 nm and capable of holding bountiful of nutrient ions due to their high surface area and release it slowly and steadily that commensurate with crop demand [7]. The application of nanofertilizers consists of N, P, K and micronutrients enhance the uptake and use of nutrients by grain crops [8].

The aim of this article is to provide a chemical synthesis which allows us to prepare CNTs easily and inexpensively either alone or loaded with NPK at low temperature without applying any pressure.

2. Materials and Methods

2.1. Materials and Chemicals

Graphite powder (Purity >99.99%) was obtained from Sigma Aldrich, Germany. potassium chlorate (KClO_3), nitric acid (HNO_3) and sulfuric acid (H_2SO_4 , 99.9 %), Calcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), urea ($\text{CO}(\text{NH}_2)_2$) and potassium chloride (KCl) were obtained from different local manufacturers and suppliers.

2.2. Preparation of Carbon Nanotubes

5 g of graphite powder was slowly added to a mixture of fuming 25 cm^3 nitric acid and 50 cm^3 sulfuric acid and stirred for 30 minutes. Then, the mixture was cooled at 5°C in an ice bath, about 25g of potassium chlorate was added slowly to the previous solution with stirring for 30 minutes. The solution was then heated at 70°C for 24 hours and then placed in the air for three days. The floating graphite carbons were rinsed with 1000 cm^3 deionized water, stirred for 1 hour, filtrated and the sample then was dried [9].

2.3. Loading of NPK Fertilizer in Carbon Nanotubes

Urea, calcium phosphate and potassium chloride were used as sources of N, P and K, respectively. The loading of NPK fertilizers on carbon nanotubes surface was obtained by dissolving about 0.2 g of N, 0.05g of P and 0.2 g of K into 50 cm^3 of carbon nanotubes solution for 6 h at room temperature [10].

2.4. Characterization of the CNTs and CNTs Loaded with NPK

2.4.1. Ultrastructural Studies Using Transmission Electron Microscope (TEM)

The morphology and size of the CNTs and CNTs- NPK were investigated using a JEOL 1010 transmission electron microscope at 80 kV (JEOL, Mansoura University). CNTs solution was sonicated for 2 minutes to produce better particle dispersion and to prevent the nanotubes accumulation on the copper grid. One drop of the solution was spread onto a carbon-coated copper grid and was then dried at room temperature for transmission electron microscopy (TEM) analysis. The sizes of the nanotubes were determined directly from the figure using an Image - ProPlus 4.5 software. The value is an average size of five parallels.

2.4.2. Ultrastructural Studies Using Scanning Electron Microscope (SEM)

According to Nallamuthu et al. [11]; a GSM 610 LV Scanning Electron Microscope was used to make surface and subsurface (up to $5\text{ }\mu\text{m}$) morphology. About 20 mg CNT sample was coated with 40 - 60 nm of gold using ion sputter and then examined with Scanning electron microscope at an accelerating voltage of 30 kV (GSM, EM. Mansoura University).

2.4.3. Electron Diffraction Analysis

Electron diffraction (ED) was performed to determine the

structure of prepared carbon nanotubes. In selected area electron diffraction, a parallel beam is used to illuminate the specimen and the diffraction pattern that is formed in the back focal plane consists of sharp spots. In this method the region of interest is selected by inserting an aperture in the first image plane of the objective lens (the selected-area aperture). When a focussed, convergent beam illuminates the specimen the diffraction pattern consists of discs. The area from which the diffraction information comes is that illuminated by the electron beam [12, 13]. All CNT diffraction patterns were obtained using a JEOL 1010 transmission electron microscope (JEOL, Mansoura University).

2.4.4. Measurement of Zeta Potential of CNTs Either Alone or Loaded with NPK

The zeta potentials of CNTs either alone or loaded with NPK were measured on zeta sizer (Malvern Instruments Ltd, EM. Mansoura University). The zeta cell should be washed by water followed by ethanol and finally by water again, dried using a gentle stream of nitrogen to remove any remaining solvent and then was covered to prevent any dust contamination. The CNTs samples were inserted to the zeta cell by gently depressing by using 1 cm^3 syringe. About three runs for each sample were performed to create measurement repeatability. The applied voltage was set automatically [14].

2.4.5. FT-IR Analyses of CNTs Either Alone or Loaded with NPK

The FTIR measurements were performed by mixing 3 mg of sample with 100 mg KBr (spectrally pure), then were pressed for 10 min under vacuum, forming a grayish round disk and measured on a Fourier transform spectrometer (NICOLET IS10 FT-IR instrument) [15].

3. Results and Discussion

3.1. Preparation of Carbon Nanotubes

Graphite powders are usually used as raw materials for bulk production of graphene sheets. Potassium chlorate with fuming nitric acid and sulfuric acid have been used to oxidize graphite into graphene oxide; nitric acid has been reacted with aromatic carbon surfaces which resulted in various oxygenated functional groups such as carboxyls, lactones, ketones, in carbon nanotubes and meanwhile, releasing of toxic gases like NO_2 and N_2O_4 . Also, potassium chlorate provides its oxidation capability by *in situ* generating dioxygen that is very reactive [16; 17; 18].

CNTs show higher adsorption capacity due to their highly porous and hollow structure, large specific surface area, hydrophobic surfaces and strong interaction between CNTs and fertilizers molecules [19]. Their adsorption ability is attributed to (i) presence of high energy adsorption sites, such as CNT defects, functional groups, and interstitial and groove regions between CNT bundles. These adsorption sites commonly exist on as-grown CNTs [20]; (ii) condensation, such as surface and capillary condensation of gas or liquid adsorbates [21]. So, when the fertilizers were dissolved in

water, cation and anion were developed then they were absorbed in the CNTs surface.

3.2. Characterization of the CNTs and CNTs Loaded with NPK Fertilizers

3.2.1. Physical Characterization

(i) Shape and structure of CNTs

To characterize the shape and structure of prepared CNTs, GSM 610 LV Scanning Electron Microscope (SEM) was used. As shown in figure 1a, CNTs had sharp edges and exhibit several sheets.

(ii) Morphology and size of CNTs and CNTs loaded with NPK fertilizers

TEM micrographs were taken to investigate the morphology of the prepared CNTs. In figure 1b; long and stripe-like CNTs are distinctly visible. The diameter of CNTs increase from 15.8 to 78.43 nm that indicated that the type of CNTs is multiwalled (MWCNTs).

Careful examination of figure 1c, d and e reveals that the addition of N, P or K to nanotubes solution leads to increase the sizes of nanotubes. The maximum increase in the mean diameter was 186.13% with the addition of phosphorus due to the formation H_2PO_4^- and PO_4^{2-} groups of calcium phosphate, 66.71% with nitrogen due to deformation of ammonium ions ($-\text{NH}_4^+$) and 27% with the addition of potassium due to the dissociation of KCl producing K^+ ions.

(iii) Structure of CNTs

Electron diffraction is the most direct and fast technique that gives access to detailed information about the structures of carbon nanotubes [3]. The electron diffraction pattern indicates that the tube has nearly identical chirality for all of the concentric graphitic layers, as a zigzag-type MWCNT. Figure 1f show that the diffraction configurations exhibit rotation crystal patterns. Rings and spots indicating that the nanotubes contain zigzag edges and are crystallized.

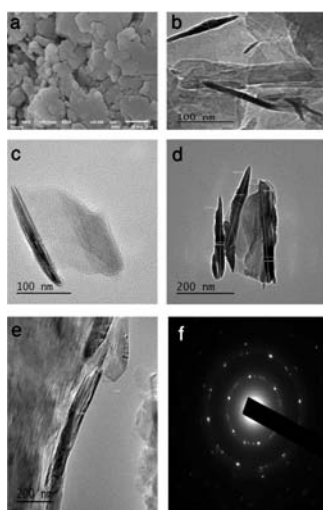


Figure 1. a- SEM micrograph of the CNTs, b- TEM micrograph of carbon nanotubes (CNT), c- TEM micrograph obtained for carbon nanotubes (CNT) loaded with urea $\text{CNT}-(\text{NH}_2\text{CONH}_2)$, d- TEM micrograph obtained for carbon nanotubes (CNT) loaded with potassium chloride $\text{CNTs}-(\text{KCl})$, e- TEM micrograph obtained for carbon nanotubes (CNT) loaded with calcium phosphate $(\text{CNT}-(\text{Ca}(\text{H}_2\text{PO}_4)_2))$, f- Electron diffraction pattern of CNTs.

3.2.2. Chemical Characterization

(i) Zeta potential (ζ)

Table 1 and figure 2 indicate the value of zeta potential (ζ) of CNTs either alone or in combination with N, P or K fertilizer according with the changing pH; It was found that for CNTs loaded with nitrogen (N), the zeta potential value (ζ) was significantly increased. The ζ value of the dispersion of CNTs loaded with phosphorus (P) was lower when compared to the ζ value of pure CNTs, and for the dispersion of CNTs loaded with potassium (K). According to the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, a potential between charged particles in suspension may result in colloidal meta-stability due to the van der-waals forces and repulsion caused by the overlap of the electric double layer around each particle [22].

The MWCNTs may possess negative or positive charge on their surface, depending if the surrounding media used is a cationic or anionic. The zeta potential is used to study the stability of carbon nanotubes. CNTs solution is more sensitive to change in the pH of medium and negative values of the zeta potential indicate that the CNTs are negatively loaded. This difference in the zeta potential values depending on the medium pH is attributed to the energy electrical field in the CNTs surface surrounded by another ion [23]. The zeta potential increase gradually, with the addition of NPK fertilizer due to the absorption of negative and positive charge on the surface of carbon nanotubes.

(ii) FT-IR analyses

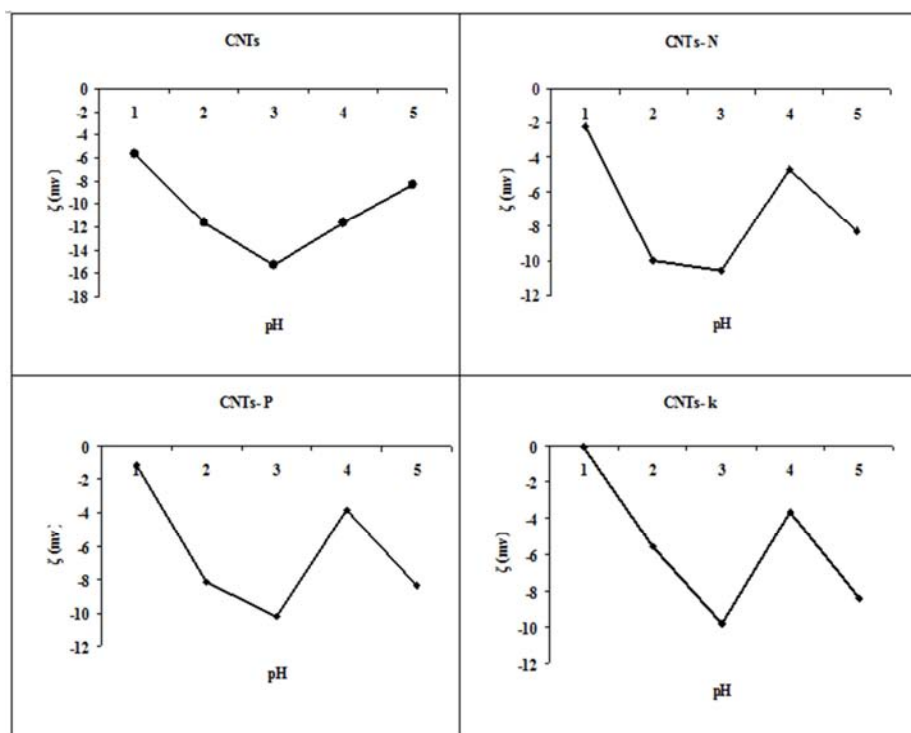
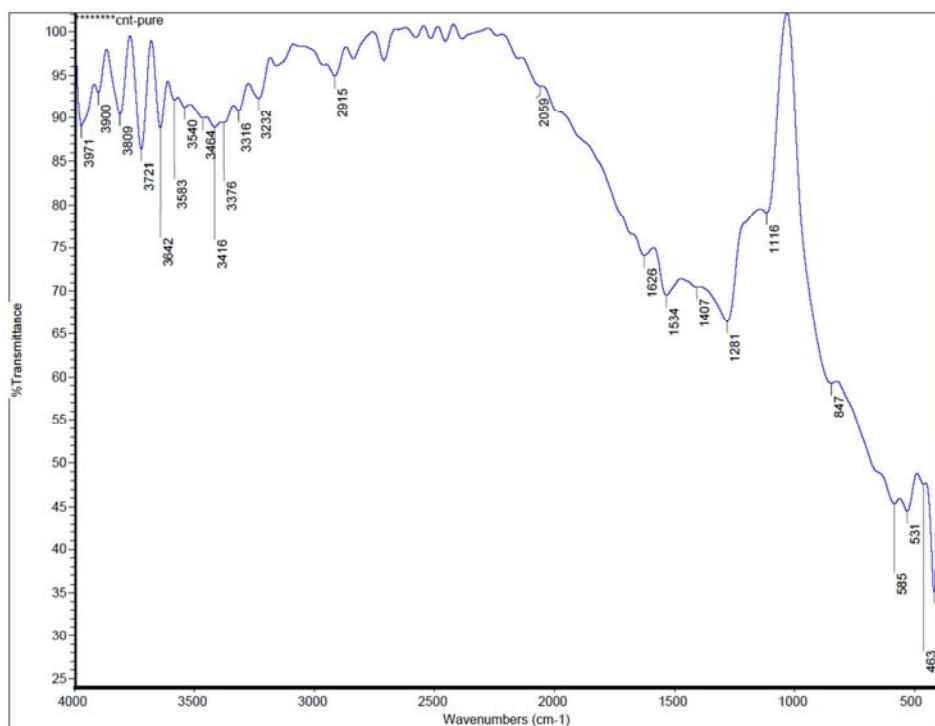
FTIR is used to study spectral changes in position or shape occurred in the distribution of frequencies which used to identify the presence of functional group absorbed by carbon nanotubes. In the measured IR absorbance spectrum, a prime intensity peak is seen at 1584 cm^{-1} . This is an IR-active, graphite originating from the sp^2 hybridized carbon [24]. Peaks at 2915 and 2854 cm^{-1} are caused by C-H vibrations of alkyl group which are a residue of hydrocarbon molecules used for growing the CNTs. The band at 3434 cm^{-1} can be attributed to vibrations of O-H bonds in hydroxyl and carboxyl groups formed upon the oxidation of the nanotubes, the absorption peaks at 1573 and 1634 cm^{-1} can be attributed to $>\text{C}=\text{O}$ groups.

IR spectrum of the CNTs oxidized with nitric acid is characterized by the presence of absorption bands corresponding to C-H (2923 , 2854 and 1462 cm^{-1}), $>\text{C}=\text{C}<$ (1636 cm^{-1}), and O-H (3450 cm^{-1}) bonds. The absorption band corresponding to the C=O bond vibration in the carboxyl (1739 cm^{-1}) in the IR spectrum of the boiling nitric acid oxidized CNTs, has a very low intensity. This peak was more pronounced for the material oxidized with nitric acid vapor. Thus, the IR data indicated that treatment of the CNTs with nitric acid vapor resulted in much more deep oxidation [25].

The presence of C-N and N- CH_3 bonds at 1391 cm^{-1} is attributed to the presence of intercalated N atoms between the graphite layers at the inner part of the nanotube walls however, may not be strongly IR active [26].

Table 1. Zeta potential (ζ) of carbon nanotubes either alone or in combination with N, P or K fertilizer depending on pH.

PH	CNT	CNTs- N	CNTs- P	CNTs-K
1	-5.70	-2.19	-1.13	-0.075
1.5	-11.7	-10.00	-8.2	-5.57
2	-15.3	-10.6	-10.2	-9.84
2.5	-11.7	-4.68	-3.8	-3.64
3	-8.32	-8.30	-8.35	-8.40

**Figure 2.** Zeta potential (ζ) of carbon nanotubes either alone or in combination with N, P or K fertilizer depending on pH.**Figure 3.** IR spectrum of pure solid CNTs.

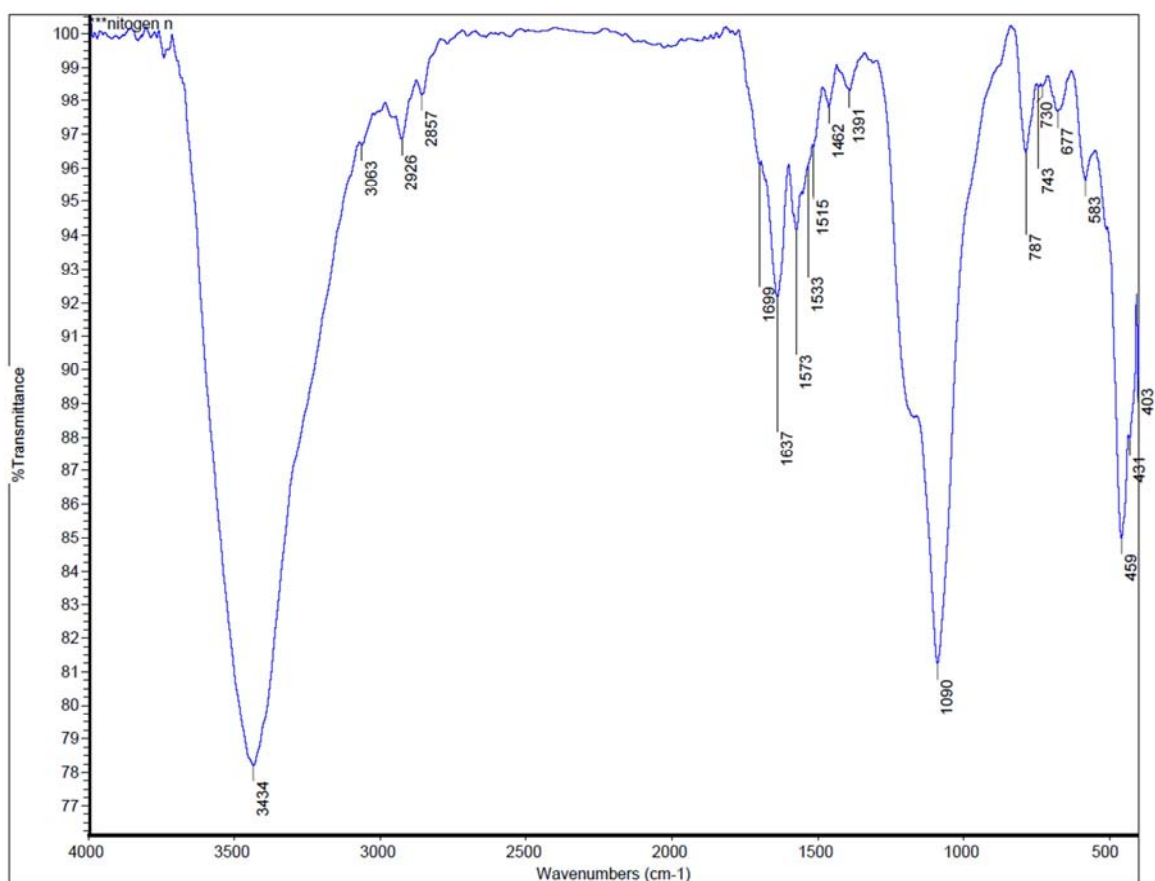


Figure 4. IR spectrum of for carbon nanotubes (CNT) loaded with urea CNT-(NH₂CONH₂).

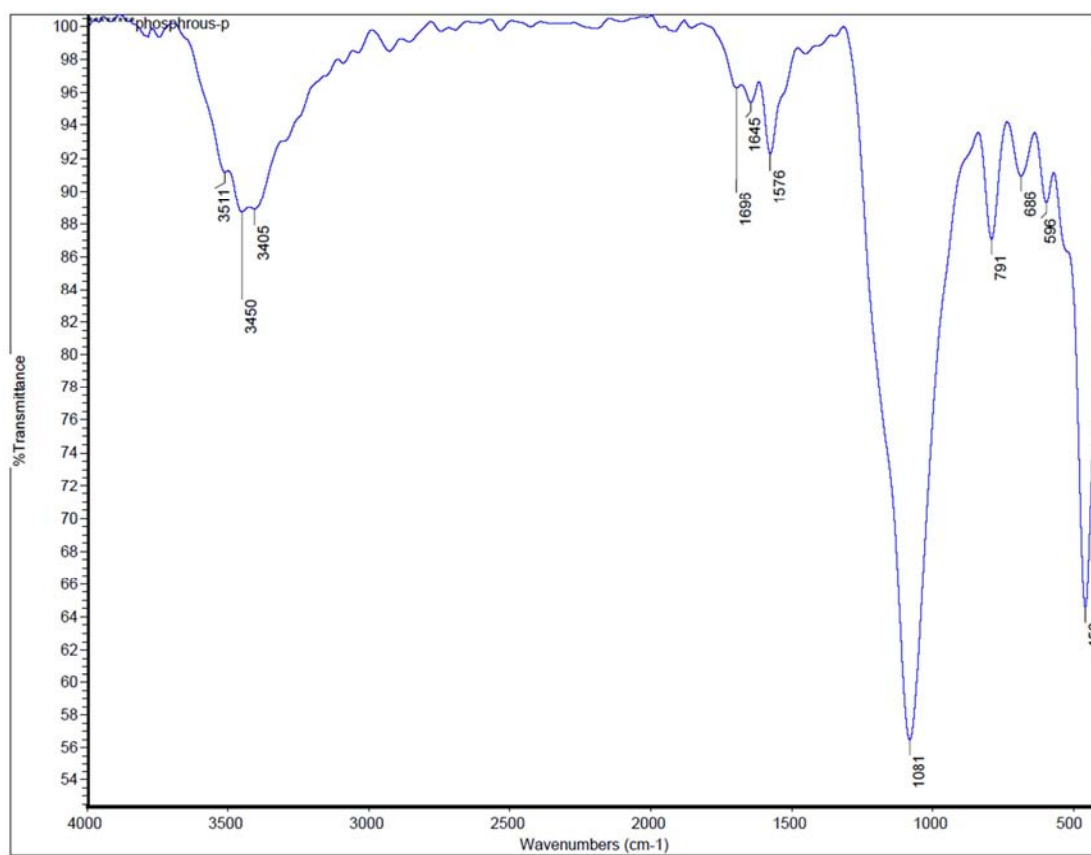


Figure 5. IR spectrum of for carbon nanotubes (CNT) loaded with calcium phosphate ((CNT-(Ca (H₂PO₄)₂)).

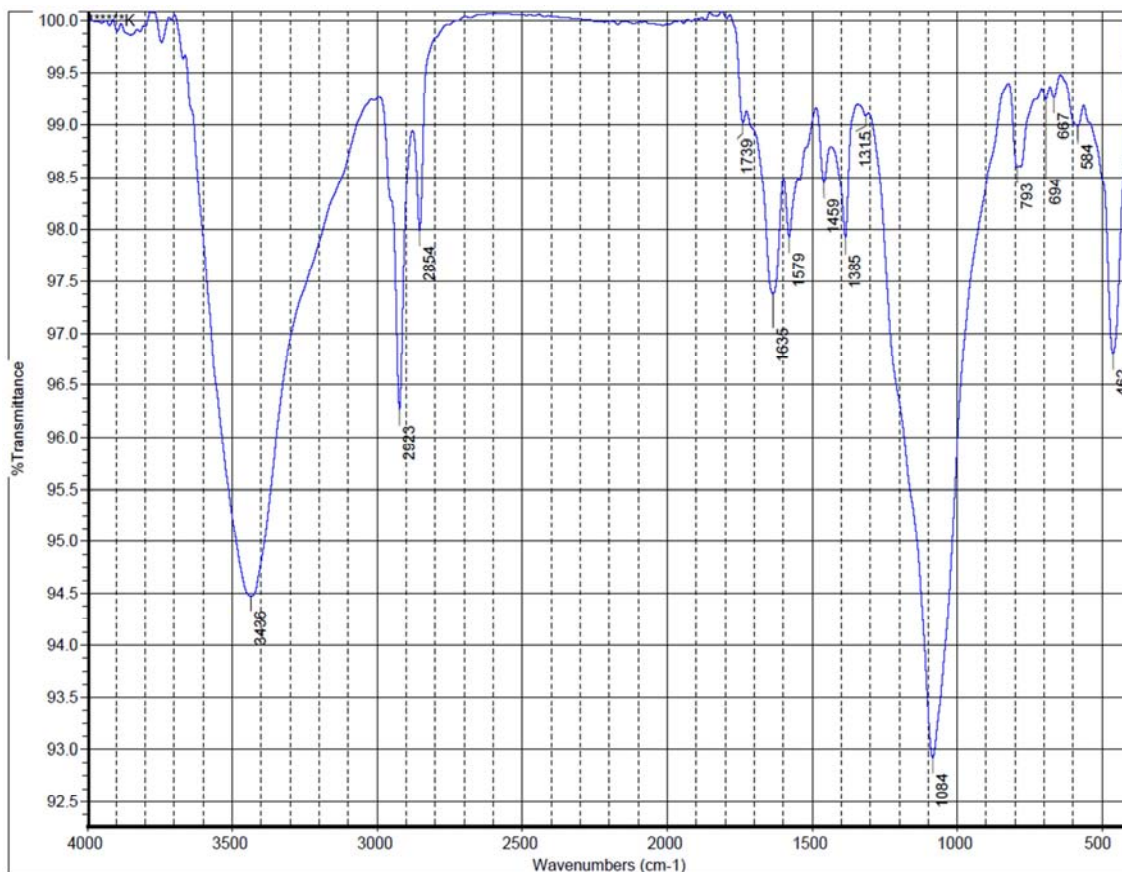


Figure 6. IR spectrum of for carbon nanotubes (CNT) loaded with with potassium chloride CNTs- (KCl).

4. Conclusion

From the provided results it is apparent that CNT have been loaded successfully with nitrogen, phosphorus and potassium which open a wide array of uses to such CNTs. The amazing findings here within can contribute to the use of such loaded CNTs as slow release fertilizers which could open up new era of agricultural uses and practices.

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