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Carbon dots from dragonfruit peels as growth-enhancer on *ipomoea aquatica* vegetable cultivation

Mahardika Prasetya Aji[1], Lathifatus Sholikhah[1], Fina Idhamatus Silmi[1], Hestining Ajeng Permatasari[1], Ita Rahmawati[1], Aan Priyanto[2] and Bebeh Wahid Nuryadin[3]

[1] Department of Physics, Universitas Negeri Semarang, Jalan Taman Siswa, Sekaran, Gunungpati Semarang, Central Java 50229, Indonesia

[2] Department of Physics, Institut Teknologi Bandung, Jalan Ganesha No.10, Bandung West Java 40132, Indonesia

[3] Department of Physics, Universitas Islam Negeri Sunan Gunung Djati, Jalan A. H. Nasution No. 105, Cibiru Bandung West Java 40614, Indonesia

E-mail: mahardika@mail.unnes.ac.id

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Abstract

C-dots have been successfully synthesised from the dragon fruit peels and were applied as growth-enhancer for *Ipomoea aquatica* vegetable cultivation. C-dots were obtained from the extract of dragon fruit peels via microwave radiation for 5 to 30 min. Two typical peaks of betalains in the dragon fruit peel extract experienced alteration. When increasing the microwave radiation time, typical peak intensity at 543 nm is decreased and peak intensity at 393 nm is increased. C-dots from dragon fruit peels have particle size in range of 8–25 nm. The optimum C-dots have been produced from 20-min microwave radiation with power of 230 watt. The emission of C-dots appeared at wavelength of 450 nm. The obtained C-dots are capable of binding nitrogen-phosphor-potassium (NPK) fertiliser and act as nutrients carrier. C-dots were then directly supplemented to *Ipomoea aquatica* vegetable to figure out their influence on plant growth. The supplementation of C-dots was varied by their volume fraction. The effect of C-dots was analysed by measuring the growth rate of plant. This study confirmed that the supplementation of C-dots could enhance the growth of *Ipomoea aquatica* vegetable. This study denoted that C-dots from dragon fruit peel extracts successfully act as a growth enhancer to increase vegetable yields.

Keywords: carbon dots, dragon fruit peels, growth enhancer, imopea aquatica
Classification numbers: 1.00, 2.10, 4.02, 5.00

1. Introduction

Nanotechnology is currently being applied in agriculture. Nanomaterials play several fundamental roles in agriculture as plant protection, fertilisation and growth promotion [1–6]. Several nanomaterials such as titanium dioxide (TiO_2) and zinc oxide (ZnO) are able to act as pesticides, fungicides, and bactericides for plants. Whereas, nanoparticles of calcium (Ca), potassium (K), zinc (Zn), phosphor (P), sulfur (S), iron (Fe), manganese (Mn) and magnesium (Mg) could also be used as nutrients to promote the plant growth [7–12]. Another significant application of nanomaterial is as an active material for nutrient deliveries and suppression of nutrient losses in fertilisation. Nanomaterials such as ZnO, gold (Au), magnetite (Fe_3O_4), carbon nanotubes (CNT), carbon nanodots (C-dots) have been successfully used to trigger seed growth, root and stem formation in plants [12–15]. Nanomaterials with their tiny size allow them to be easily absorbed by plants. In addition, they are capable of strongly binding the nutrients in the soil using the electrostatic interaction forces.

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Although nanomaterials could minimise nutrient losses in fertilisation, but several issues are still to be addressed. The inorganic nanomaterials as plant supplements can be potentially accumulated in plants and possibly harmful for consumption. Furthermore, toxicity is a crucial problem from the use of inorganic nanoparticles in fertilisation. For further development of nanomaterials for agriculture, organic materials become very promising to produce non-toxic nanomaterials. The use of organic nanomaterials in agriculture is still rare. Researcher from China successfully synthesised C-dots from pollen plant. The use of 10–30 $mg\,l^{-1}$ C-dots from pollen has successfully triggered the growth of *Lactuca sativa L.* C-dots are very promising for plant supplements due to their tiny size <10 nm, non-toxicity and easy dissolution [16]. Moreover, negative charged ligands on a surface of C-dots could act as nutrient binder for delivery process in fertilisation.

C-dots are easily synthesised from organic materials with prosperous carbon chains such as various pigments in flowers, fruit and fruit peels. Betalain pigment in the dragon fruit peels has become one of the organic materials for producing C-dots [17]. With the properties of less cytotoxicity and good biocompatibility, C-dots are very potentially useful for agriculture. In addition, another potential of betalain pigment in dragon fruit peels is the presence of nitrogen in its functional groups as a macronutrient needed by plants. In present work, we synthesise C-dots from dragon fruit peels and use it as a growth enhancer for *Ipomoea aquatica* vegetable.

2. Experiment

Ripe red dragon fruit is easily obtained from the local market in Semarang, Central Java-Indonesia. The raw material for synthesis is dragon fruit peel. Another ingredient is urea with technical quality obtained from the chemical shop in Indrasari, Indonesia. Betalain pigment was extracted by heating process of 20 g dragon fruit peels in 100 ml of distilled water at 70 °C for 2 h. A total of 20 ml of dragon fruit peel extract was mixed with 2 g of urea. A total of 20 ml of this homogeneous extract solution was then irradiated by 230 watt microwave (Panasonic NN-SM322M) for 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min. The absorption and emission spectra of C-dots from synthesis were then analysed. The absorption spectrum was measured using Vis-Nir Ocean Optics type USB 4000. While the emission spectrum was measured using a photoluminescence device of Cary Eclipse type Spectrofluorometer MY14440002. The changes in the functional groups of the dragon fruit peel extracts due to microwave radiation were analysed by measurement using Fourier transform infrared (FTIR) type Perkin Elmer Spectrum Version 10.03.06. C-dots particle size was analysed by transmission electron microscopy (TEM) (Hitachi TEM system HT7700). C-dots with optimum absorption and emission spectra were then used as growth enhancer for *Ipomoea aquatica* vegetable cultivation. The plant was grown from seeds on soil medium and under sunlight. After 5 days of growth, we selected plants with similar height and conditions for treatment at 10 × 19 × 6 cm container. Plants only receive C-dots supplementation with volume variations of 0 ml, 25 ml, 50 ml, 75 ml, 100 ml, and 125 ml in 1000 ml of distilled water without any other fertiliser. This supplementation was given every 5 days. The growth rate can be then observed in a certain period of time. During the treatment, environmental parameters—light intensity, temperature and humidity—were measured using Lightmeter LT Lutron LX-107HA and Victor VX230A respectively.

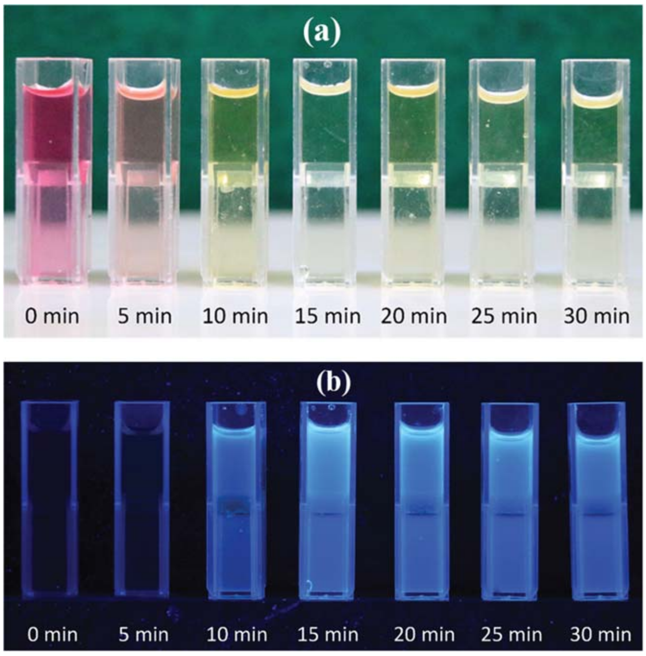

Figure 1. Dragon fruit peel extract irradiated by microwave in: (a) day light and (b) *UV* light.

3. Result and discussion

The colour of extracts of dragon fruit peels irradiated by microwave changes from red to brown as shown in figure 1. The dominant red colour of dragon fruit peel extract shows betalain pigment [18]. Microwave radiation causes polymerisation and carbonisation processes at betalain pigment, thus the extract turns into brown. This colour change denotes an alteration of the optical properties in the extract. Dragon fruit peel extract does not emit when irradiated using ultraviolet (*UV*) light. Meanwhile, dragon fruit peel extract which has been irradiated by microwave emits waves when irradiated by *UV* light. The emission shows that the extract of the dragon fruit peels irradiated by microwave yields C-dots particles. This luminescence property is also found in C-dots produced from other fruit peels—mangosteen, orange, watermelon, etc., waste plastics, leaves, sugar, flowers, and pollen seeds [16, 19–24].

Microwave radiation changes the absorbance spectrum of dragon fruit peel extract as shown in figure 2. The absorption spectrum of dragon fruit peels extract is in the wavelength range of 350–700 nm. Dragon fruit peel extract solution

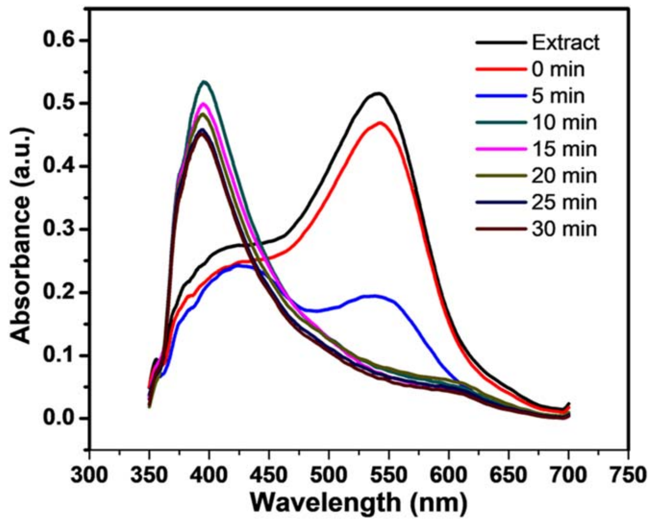

Figure 2. Absorbance spectrum of the obtained dragon fruit peel extract irradiated by microwave.

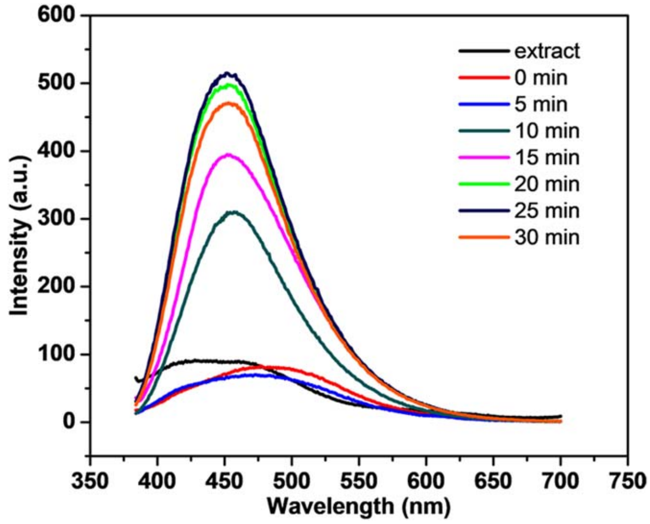

Figure 3. Photoluminescence spectrum of the obtained dragon fruit peel extract irradiated by microwave.

showed two peaks of absorbance at 393 nm and 543 nm wavelengths. Two peaks are typical of the betalain pigment in the extract of dragon fruit peels [25]. Two typical peaks of betalains in the absorbance spectrum are still observed in the extracts of dragon fruit peels which were given by microwave radiation for 5 min. When increasing the microwave radiation time, the typical peak intensity at 543 nm is decreased and peak intensity at 393 nm is increased. The energy of microwave radiation breaks the conjugate double bonds in the betalain pigment, thus the intensity at the wavelength of 543 nm has decreased. Whereas the intensity of the absorption spectrum at wavelength 393 nm goes higher with the longer time of the microwave radiation. This is related to the vibrations of the short chain bonds which are increasing due to termination of the other pigment chains.

Reduction of absorption spectrum intensity also occurs in the extract of dragon fruit peels with and without urea due to a chemical interaction between dragon fruit peel extract and

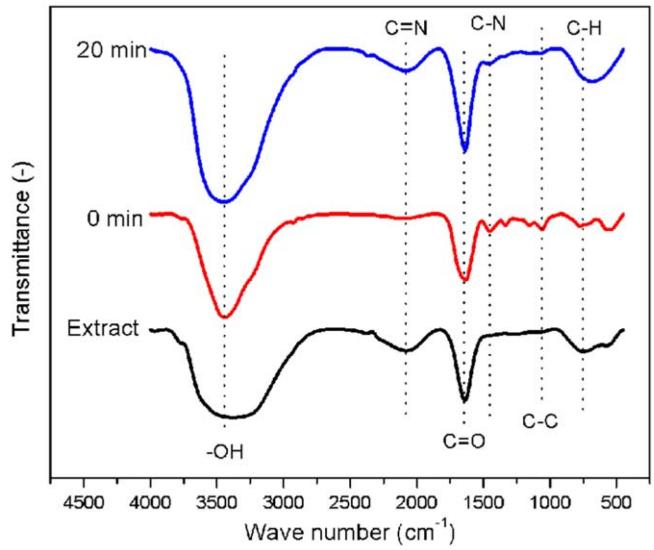

Figure 4. FTIR spectrum of the obtained dragon fruit peel extract, and irradiated by microwave for 0 min and 20 min

urea. The presence of urea in the dragon fruit peel extract is very important as passivation agent to modify the functional groups on the surface of C-dots. The typical peaks of the betalain pigment denote an electronic transition. The peak at 393 nm shows the electron transition in $n \rightarrow \pi^*$ and the peak at 543 nm denotes the electron transition in $\pi \rightarrow \pi*$ orbitals. The electron transition to the bonding $n \rightarrow \pi*$ orbitals is the electron transition from the C=C bond while the electron transition to the $\pi \rightarrow \pi*$ orbitals shows the transition from sp^2 of the C=O and C=N bonds [26–28].

The excited electrons due to C-dots receiving *UV* light experienced recombination process—returning to ground state by emitting the visible light. The C-dots photoluminescence spectrum is in the wavelength range of 375–650 nm as shown in figure 3. The C-dots photoluminescence peak is at a wavelength of 450 nm (1.92 eV). The enhancement of photoluminescence intensity occurred in the spectrum of the extract before being irradiated with microwave to the extract after being irradiated for 20 min. The higher intensity indicates the larger number of C-dots produced from dragon fruit peels . Thus, 20 min is an effective radiation time in the mechanism of formation of C-dots from dragon fruit peel extract. C-dots that are produced from 20-min radiation are then applied as a supplementary growth enhancer of *Ipomoea aquatica* cultivation. The intensity of photoluminescence of dragon fruit peel extract decreases when irradiated for 30 min where C-dots turn into carbon charcoal.

The photoluminescence mechanism of C-dots from dragon fruit peels is influenced by the electronic transition π. The electrons in the highest occupied molecular orbital (HOMO) band are excited to the lowest unoccupied molecular orbital (LUMO) band after receiving *UV* energy outside. The electrons in the LUMO band are unstable, so they recombine into the HOMO band by emitting visible light.

The alteration of functional group of dragon fruit peel extract irradiated by microwave for 20 min is shown by the

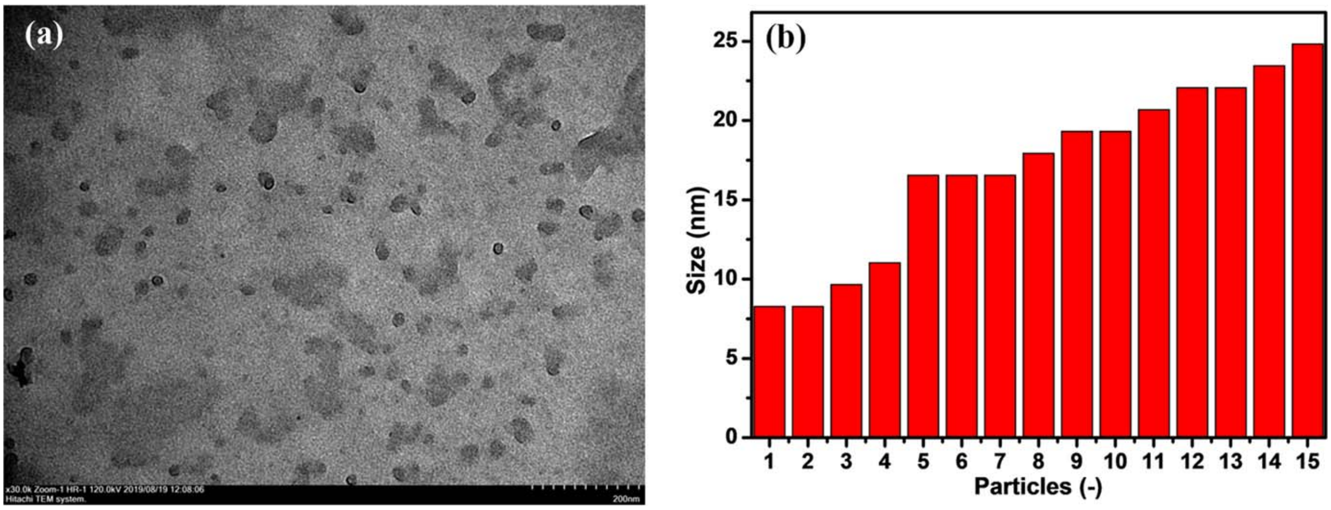

Figure 5. (a) TEM image of 20-min synthesised C-dots, (b) particle size distribution of 20-min synthesised C-dots.

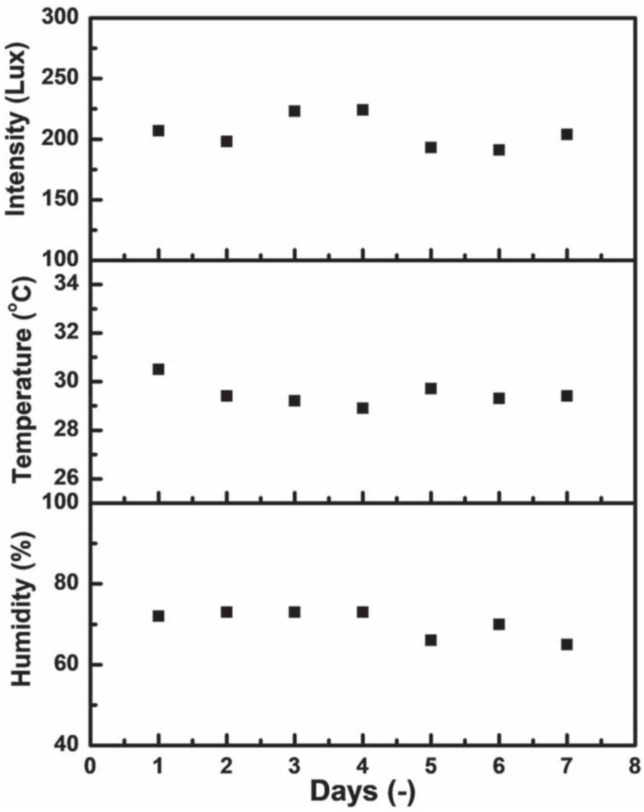

Figure 6. Measured environmental parameters during treatment.

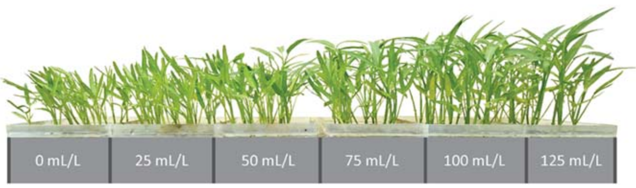

Figure 7. Growth of *Ipomoea aquatica* plants with various volumes of C-dots after 20 days.

FTIR analysis in figure 4. The wavenumber band of 729 cm^{-1} indicates a strong bending of C–H. The band shows changes in spectrum patterns that indicate damage of the aromatic structures in the pigment caused by microwave radiation. The functional group of OH-stretching is found in the absorption area of 3478 cm^{-1} which denotes the presence of water (H_2O) as a solvent. The band at wavenumber of 1639 cm^{-1} shows the bond of C=O. In addition, the bond of C=N appears at wavenumber of 2123 cm^{-1} [21]. C–H, C=O, and C=N bonds are functional groups formed on the surface of C-dots. The C=N bond signifies that the addition of urea has successfully modified the surface structure of the C-dots from the extract of the dragon fruit peels.

TEM image of 20-min synthesised C-dots is shown in figure 5. C-dots particles have size distribution in range of 8–25 nm. Generally, C-dots from organic materials such as pollen, watermelon, sugar, rose flower, etc have size distribution $<$10 nm [16, 21, 23, 24]. TEM image in figure 5 shows that C-dots experienced agglomeration due to surface interaction between C-dots particles [29].

The obtained C-dots have size in nanometers, which is very promising for absorption process in fertilisation. *Ipomoea aquatica* was chosen for C-dots performance as growth enhancer since they are easily to grow in both soil and water media. Furthermore, *Ipomoea aquatica* vegetable has short period of growth and is immune to several insects. *Ipomoea aquatica* that has been grown from seeds is then given a solution containing C-dots with various volume fractions. During the growth process of *Ipomoea aquatica*, environmental parameters of humidity, temperature and light intensity were measured as shown in figure 6.

Treatment was conducted under relatively stable environmental parameters. The plants were grown under temperature of 28.9 °C–30.5 °C, 65%–73% humidity and light intensity at 191 lux-224 lux.

Ipomoea aquatica grows taller with the supplementary C-dots as shown in figure 7. Generally, supplementation of

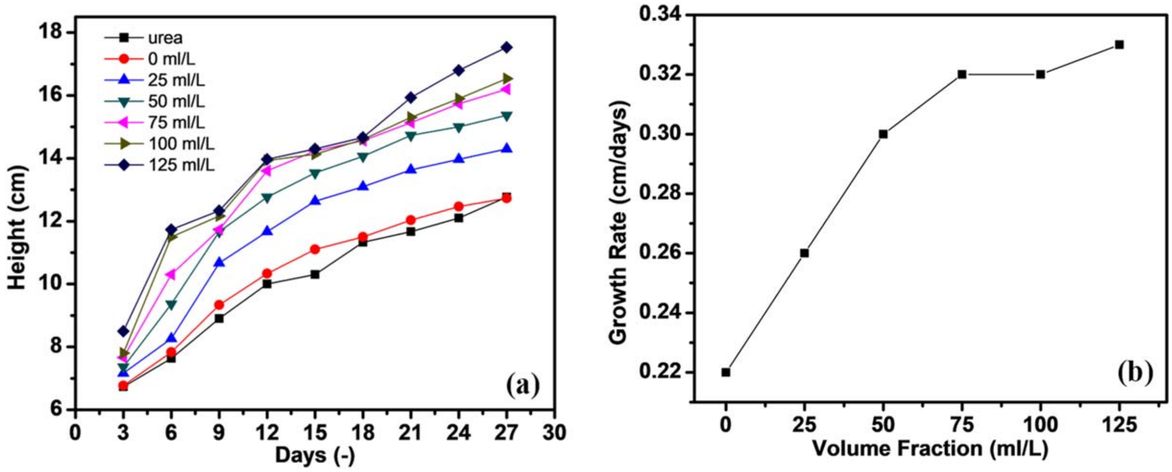

Figure 8. Effect of supplementary C-dots on *Ipomoea aquatica* physiology: (a) plant height (b) plant growth rate.

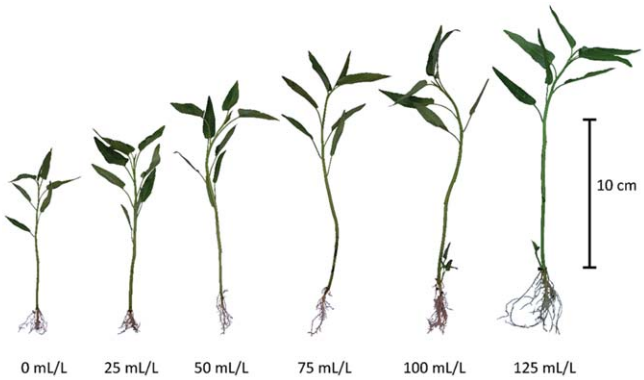

Figure 9. Effect of supplementary C-dots on the physiology of *Ipomoea aquatica* after 30 days of growth.

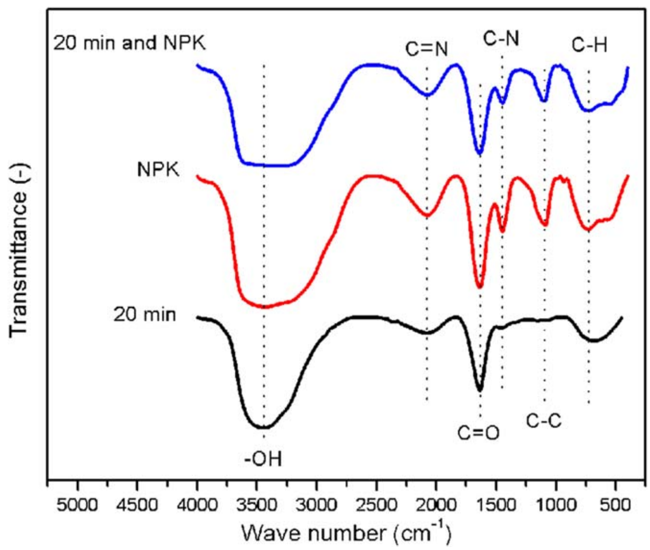

Figure 10. FTIR spectrum of the obtained dragon fruit peel extract with 20-min microwave irradiation (C-dots) with NPK.

C-dots at $125\ \mathrm{ml\,l^{-1}}$ yields higher plant. High volume of supplementation leads to high absorption of C-dots by plant through plant transport mechanisms.

The effect of supplementary C-dots on the height of vegetable is shown in figure 8(a). The results showed that *Ipomoea aquatica* with supplementary C-dots grew taller than that without C-dots, and also taller than vegetables which were only given urea. In addition, the greater the volume of supplementary C-dots, the taller the vegetable grows . The effectiveness of C-dots as growth enhancer is described by the growth rate as shown in figure 8(b). The growth rate of *Ipomoea aquatica* goes with a positive trend. However, growth rates did not differ significantly when fertilised with a volume fraction of $100\ \mathrm{ml\,l^{-1}}$. This indicates that the volume fraction of $100\ \mathrm{ml\,l^{-1}}$ is the limit of the saturation volume of C-dots given to the plant.

The yield and physiology of *Ipomoea aquatica* due to the supplementary C-dots are shown in figure 9. Higher volume of C-dots yields vegetable with thicker and longer roots, longer leaves, and taller stems. This indicates that C-dots from dragon fruit peels can be effectively used as a growth enhancer of *Ipomoea aquatica*.

The interaction of C-dots with NPK fertiliser is shown in figure 10. NPK has a C–N functional group at wavenumber of $1483\ \mathrm{cm^{-1}}$. Whereas C-dots from dragon fruit peels have no C–N functional group at these wavenumbers. The intensity of the C–N functional group was more clearly observed in the mixing of C-dots and NPK. This indicates that there is an interaction between C-dots and NPK, and C-dots can bind NPK so that it can be potentially useful as a nutrient carrier.

4. Conclusion

In this work, C-dots have been successfully synthesised and implemented as growth enhancer for *Ipomoea aquatica* vegetable cultivation. The optimum C-dots have been obtained from the extracts of dragon fruit peels irradiated by microwave for 20 min. The obtained C-dots are capable binding NPK fertiliser and act as nutrient carrier. It was confirmed that the supplementation of C-dots enhances the growth of *Ipomoea aquatica* vegetable. This study denoted that C-dots from dragon fruit peel extracts successfully act as a growth enhancer to increase vegetable yields.

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