

## Research Article

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**Nor Nadiah Abdul Hamid, Noraiham Mohamad, Lum Yip Hing, Mohd Fairuz Dimin**

*Engineering Materials Department, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia*

**Mohd Asyadi Azam, Mohd Haneesyah Che Hassan, Mohd Khairul Shahril Mustaq Ahmad, Azizah Shaaban**

*Engineering Materials Department, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia*

**Correspondence:**  
**Noraiham Mohamad**

*Engineering Materials Department, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia*

**Tel:** +606-331-6976

**Fax:** +606-331-6411

**E-mail:** [noraiham@utem.edu.my](mailto:noraiham@utem.edu.my)

## The effect of chitosan content to physical and degradation properties of biodegradable urea fertilizer

*Nor Nadiah Abdul Hamid, \*Noraiham Mohamad, Lum Yip Hing, Mohd Fairuz Dimin, Mohd Asyadi Azam, Mohd Haneesyah Che Hassan, Mohd Khairul Shahril Mustaq Ahmad, Azizah Shaaban*

### Abstract

Chitosan has been widely used in many applications due to its biodegradability and non-toxicity. This article discusses the effect of different chitosan loadings on properties of urea fertilizer which prepared through direct wet mixing process. Absorption and soil degradation tests were performed to measure the amount of water intakes and the life-cycle of the fertilizer. The chemical interaction and thermal properties were analyzed using FTIR and DSC, respectively. It was found that water absorbency and degradation rate increases with chitosan loading, and FTIR confirms the presence of urea in as-produced fertilizers from a unique  $-NH$  and amide  $C=O$  functional groups.

**Keywords:** Chitosan, Urea Fertilizer, Degradation, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC).

### Introduction

Fertilizer is a chemical compound containing three elements which are nitrogen, phosphorous and potassium. It is added to soil to release nutrients which are essential for growth and development of crops. There are various types of fertilizer either organic or synthetic fertilizers. An important synthetic fertilizer is urea fertilizer; a major source of nitrogen nutrient for plants.<sup>1</sup> Unfortunately, the practical use of this fertilizer is not efficient due to the loss during application. Potential hazards of fertilizers to the environment have resulted in limitation of their use. The used of conventional fertilizers may lead to concentration levels that are too high for effective action. High concentration fertilizer may produce undesirable side effects either in the target area, which could lead to crop damage, or in the surrounding environment.<sup>2</sup> Therefore, it is important to improve its performance during utilization process. To address these problems, slow and controlled-release technology in fertilizer is considered as a suitable method to efficiently supply nutrients to plants and at the same time to decrease the loss and contamination. The technology is designed for the fertilizer to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant. These properties can be physically imparted in fertilizers by coating techniques on granule of conventional fertilizers with various materials that reduce their dissolution rate.<sup>3, 4</sup>

Urea formaldehyde (UF) is an example of a commercial, widely used and slowly soluble synthetic organic fertilizer compound.

Urea fertilizer is one of the nitrogen fertilizers with the highest nitrogen content.<sup>5</sup> Mixture of urea and formaldehyde contains combination of unreacted urea, short and long chain methylene polymers, and other trace compounds.<sup>6</sup> Once applied to plants, UF availability depends on dissolution process before microbial decomposition. One important limitation of UF is it will not react with plants in a dry and/or cold soil. Therefore, it should only be applied to the soil which biologically active. Formaldehyde is a highly reactive one-carbon compound with unpleasant characteristic odour in air at only 0.1 – 1.0 ppm concentration range. In the presence of water, formaldehyde reacts with active hydrogen of most compounds such as ammonia, amines, amides, thiols, phenols and nitro-alkanes and condenses with hydrogen chloride in the presence of water to form chloromethyl ether. Most of these abovementioned reactions are known as carcinogen in humans and animals.<sup>7, 8</sup> Formaldehyde is known to cause watery eyes, burning sensations in the eyes, nose and throat, nausea, coughing, chest tightness, wheezing, skin rashes, and allergic reactions to humans once exposed at certain level. The worst case, it can cause nasal cancer once over exposed at a high concentration volume. Recently, formaldehyde is widely used in agriculture technology as a non-biodegradable binder. It can dissolve in water and leach through the soil. Retention of this highly toxic substance has high potential to kill most of the soil organisms.<sup>9, 10</sup>

Biodegradability has become a key factor in fertilizer's technology towards a sustainable agriculture. Biodegradation is a natural process in which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles by micro-organisms activity.<sup>2</sup> Biodegradable polymer binder is new promising candidate to be used as replacement of formaldehyde as anti-caking and slow release agent in fertilizers industry. Although there are large numbers of available synthetic biodegradable polymer binders in the market such as polyethylene glycol, polycaprolactam, polyvinyl alcohol, poly (lactide-co-glycolide), etc., however, it is less practical to be used in agriculture products due to expensive prices.

On the other hand, chitosan is a natural biodegradable based polysaccharide with amine groups. It is a highly deacetylated derivative of chitin, one of the most abundant natural and biodegradable polymers that have been widely applied in the biomedical, pharmaceutical, and agricultural fields. In many of these applications, chitosan is attractive

due to its biodegradability, biocompatibility, and non-toxicity.<sup>4, 12</sup> Chitosan is one of unique materials which easily undergo biodegradation in natural environment, highly biocompatible and having unique polycationic properties.<sup>12</sup>

Nowadays, chitosan has drawn tremendous attention among researchers in the field. There are various studies regarding chitosan and its natural resource (shrimp shell); particularly in nano-particles<sup>13</sup>, shrimp shell filled recycled polypropylene<sup>14</sup>, PVOH/chitosan-blended films<sup>15</sup>, mechanism of chitosan degradation by gamma and e-beam irradiation<sup>16</sup>, FTIR studies of chitosan<sup>17-19</sup> as well as chitosan as biosensors.<sup>20</sup> In this paper, we report the potential of chitosan to replace formaldehyde in urea fertilizer. This manuscript will first discuss the preparation of chitosan based urea fertilizer, and then followed by the characterization as to analyze the effect of chitosan loading to physical, thermal and chemical properties.

## **Materials and Methods**

### **Raw Materials**

Chitosan powders (419419 Aldrich) with particle size between 1.32- $\mu\text{m}$  – 590.10- $\mu\text{m}$  were purchased from Sigma Aldrich. Industrial grade bentonite with particle size of 1.32- $\mu\text{m}$  – 83.71- $\mu\text{m}$  and urea powder (QReC) with particle size of 5- $\mu\text{m}$  – 590- $\mu\text{m}$ ) and molecular weight of 60.06 gmol<sup>-1</sup> were supplied by local company. Table 1 shows composition of main raw materials in the fertilizer.

### **Preparation of chitosan based urea fertilizer (CBUF)**

Samples were prepared through direct wet mixing method using an experimental set up which consist of beaker, hotplate and magnetic stirrer. Chitosan and bentonite were put in a beaker and stirred together in 10 ml distilled water at 60°C using magnetic stirrer at 300 rpm until gelatinization. Then, urea was added to the mixture and stirred until it was well blended for 20 minutes. Next, the mixture was poured into an aluminium mould and left to harden for 12 hours at room temperature ~ 25 ± 5 °C. Then, it was removed from the mould and dried in a conventional oven at 60°C for 8 hours. Further testing was performed to the samples after one day conditioned at room temperature.

As shown in Table 2, five formulations of different chitosan content were prepared at constant amount of water and urea. In the formulation, bentonite was varied according to chitosan loading to achieve the same sample's

weight of 20 g. It served as the backfill materials in the fertilizer.

**Table 1:** Composition of raw materials

Raw Material	Chemical Formula	Carbon, C (%)	Nitrogen, N (%)	Oxygen, O (%)
Chitosan	C <sub>12</sub> H <sub>24</sub> N <sub>2</sub> O <sub>9</sub>	22.40	46.84	30.75
Urea	CO(NH <sub>2</sub> ) <sub>2</sub>	55.35	6.37	38.29
Bentonite	Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> H <sub>2</sub> O	Oxygen, O (%)	Aluminum, Al (%)	Silicon, Si (%)
		52.78	12.52	34.70

**Table 2:** Formulation of chitosan based urea fertilizers

Sample Code	CBUF 1 (0.5%)	CBUF 2 (0.75%)	CBUF 3 (1.0%)	CBUF 4 (1.25%)	CBUF 5 (1.5%)
Urea (g)	18.40	18.40	18.40	18.40	18.40
Chitosan (g)	0.10	0.15	0.20	0.25	0.30
Bentonite (g)	1.50	1.45	1.40	1.35	1.30
Water (ml)	10.00	10.00	10.00	10.00	10.00

### Water Absorption

Water absorption was carried out to determine the amount of water absorbed by the samples at certain amount of time.<sup>21</sup> A piece of folded tissue paper was kept in a Petri dish with internal diameter of 5.5cm containing 6ml of purified water. Sample with initial weight of W<sub>1</sub> was placed on the tissue paper and allowed to wet completely for 60 seconds. The wetted sample was removed and reweighed (W<sub>2</sub>). Water absorption (WA) percentage was determined according to the Equation 1 where W<sub>1</sub> and W<sub>2</sub> are the weight before and after water absorption, respectively.

$$\text{Water absorption, WA (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Equation 1

### Soil Degradation Test

According to Han et al.<sup>22</sup>, fertilizer granules should undergo testing for degradation in soil which determine the life cycle of fertilizer that could affect the plant and ensure the degradation rate. Biodegradability of the samples in soils was studied by evaluating percentage weight loss of the samples.<sup>23</sup> In this study, samples with dimension of 10 mm diameter and 5 mm thickness were weighed and placed in beakers containing agricultural soil (Fig. 1). The initial weight of each beaker (W<sub>i</sub>) before samples were left for 20 days at ambient condition was recorded. Then, the current weight of the beakers was taken every day after 24 hours (W<sub>d</sub>). Degradation rate was determined by the decrease in weight with time which directly represented by weight loss (WL) in Equation 2.

$$\text{Weight Loss, WL (\%)} = \frac{W_i - W_d}{W_i} \times 100$$

Equation 2



**Figure 1:** Samples for soil degradation test

### Differential Scanning Calorimetry (DSC)

Thermal properties of fertilizers were obtained using a Differential Scanning Calorimetry (DSC; Pyris Jade from Perkin-Elmer). The analysis was carried out at temperature range of 40 °C to 150 °C and heating rate 10 °C min<sup>-1</sup>. An empty pan was used as reference during the measurement. Initial samples weights were set in the range of 5 mg – 10 mg each. In this study, DSC was carried out to support the biodegradability studies. The melting temperature and enthalpy transition loss percentage ( $\Delta H$  %) was determined using Equation 3;  $H_1$  is the enthalpy before degradation and  $H_2$  is the enthalpy after degradation.

$$\text{Enthalpy Transition Loss, } \Delta H (\%) = \frac{H_2 - H_1}{H_1} \times 100$$

Equation 3

### Fourier Transform Infrared (FTIR) analysis

FTIR (FT/IR-6100; JASCO) analysis was conducted to confirm the presence of urea in the fertilizer samples. Functional groups of chitosan based urea fertilizer were determined using FTIR which is known as a powerful tool for identifying type of chemical bonds and functional groups in a molecule by producing infrared absorption spectrum. Fertilizer granules were dispersed in dry KBr powder and ground to obtain fine particles. All spectra were recorded at ambient temperature and the analysis was performed at wavelength range from 349.05 cm<sup>-1</sup> to 4,000.60 cm<sup>-1</sup> at scanning speed of 2 mm s<sup>-1</sup> with aperture size of 7.1 mm.

## Results and Discussion

### Water Absorption

First, we discuss the water absorption analysis of all samples at different chitosan loading (Fig. 2). The amount of absorbed water increases as the amount of hydrophilic component increases in a compound. However, weight difference increases as chitosan loading increases except at the highest chitosan loading in CBUF 5 (1.5% chitosan). It is clearly observed that high chitosan loading (1.5 %) in the fertilizer had significantly reduced the obtained weight difference. This might be due to the compensation of weight gained from water absorption by weight loss due to urea release in aqueous environment. This reflects to the high dependency of water absorption capacity with hydrophilic properties of chitosan, and is in good agreement with Liang et. al.<sup>24</sup> which reported that water absorbency of polymer depends on the amount of

hydrophilic groups. In the formulation, 1.5 % chitosan had attracted enough water molecules to swell the fertilizer and cause urea to diffuse into the absorbed water and may also experience urea lost to the surrounding. Besides, the change of physical form of urea from solid to liquid also affected the weight of the final sample. This results in reduction of water absorption of this formulation since urea was the major component in the formulation.

However, for formulations less than 1.5 % chitosan, the absorbed water was only enough to cause the swelling of the chitosan itself which contributes to the gaining of its weight. Although clays such as bentonite, ball clay, kaolin and etc. has tendency to store water molecules in between of their layered structures, however, it was not the significant contributor to the water absorption in this study since its amount decreases as the chitosan amount increases in the formulation (Table 2). Water absorbency is an important criterion for slow release fertilizers<sup>4</sup> since presence of water will cause a gradually release of urea to environment. However, water absorption should be blended together with water retention since the probability of fertilizers to decompose would be very high without significant water retention ability. Nonetheless, it is important to note that the water retention property was not covered in this paper.

### Soil Degradation Test

Fig. 3 depicts the degradation rate of fertilizers based on weight loss percentage in 20 days. From day 1 to day 14, sample degraded at an accelerated pace and slowly degraded after 15 days and began to rupture at day 20 (Fig. 4). After 14 days, the samples appeared brittle and decreased in size. This visual observation is consistent with the very low rate of degradation which took place starting on day 15 until day 20 (Fig. 3). It can be suggested that the weight loss experienced by the fertilizers can be solely due to the constant environmental factors and microbe's activity which breaks down the fertilizer.<sup>25</sup> This is because there was no additional of water into the soil except for the moisture content (~ 50 %) in the environment. The degradation rate is observed to occur very rapidly in the first four days and decreases with time until the whole weight of samples were degraded.

Molecular degradation is promoted by enzymes and can occur under aerobic and anaerobic conditions, leading to complete or partial removal from the environment.<sup>25</sup> Furthermore, the percentage of weight loss is directly proportional to the chitosan content except when the

chitosan was added more than 1.25 wt% in the formulations. At this stage, the samples had shown significant reduce in the weight loss if compared to other

samples. This might be due to the significant interaction between chitosan and urea when the chitosan has added at this level.

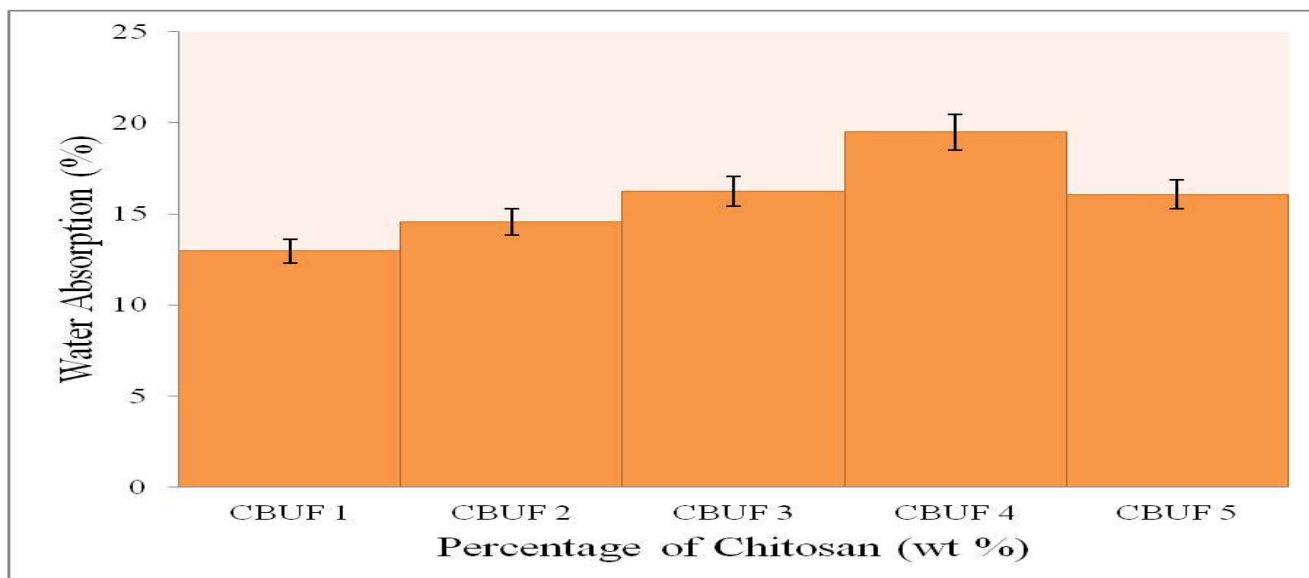


Figure 2: Water absorption of fertilizer samples at various chitosan percentages

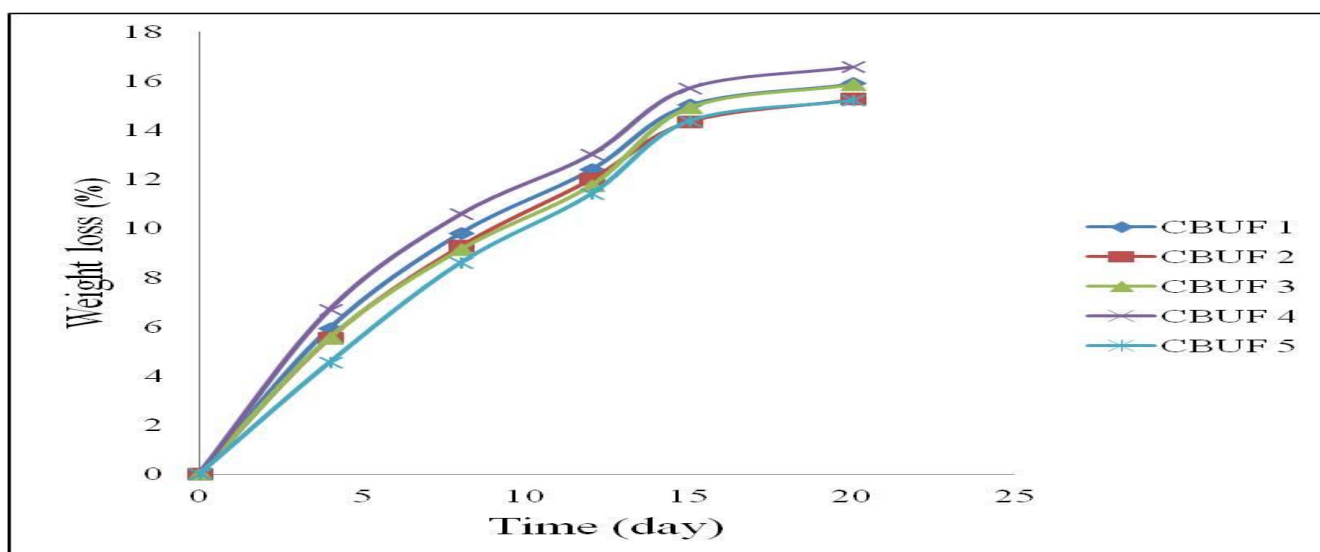


Figure 3: Weight loss of chitosan based fertilizer samples after soil degradation test for 20 days



Figure 4: White and black image of chitosan based sample degradation for (a) after 1 day (b) after 14 days and (c) after 20 days. White region is fertilizer whereas black region is the agriculture soil

### Differential Scanning Calorimetry (DSC)

The summaries of thermal properties of chitosan based urea fertilizer are tabulated in Table 3. The values of melting temperature ( $T_m$ ) and total enthalpy loss ( $\Delta H$ ) obtained for these samples before and after soil degradation study reflect to the level of biodegradation reaction occurred on the samples. In the case of polymer degradation and/or or reduction of its molecular mass, the decrease of the melting temperatures is shown in Fig. 5. In addition, decrease of enthalpy also indicates amorphous phase degradation and, consequently, crystalline regions, which results in polymer material destruction.<sup>26</sup> The examination results imply that chitosan based fertilizers experienced almost 80 % degradation after 20 days which depicted by the value of  $\Delta H$  of around  $83 \pm 2\%$  for every sample regardless of the percentage of chitosan loading.

This observation confirms the presence of higher chitosan loading had contributed to slightly increase in degraded weight per time but the effect is trivial. This is proved by the insignificant difference observed in  $T_m$  and  $\Delta H$  of these samples. Furthermore, it shows the presence of chitosan has negligible contribution to the disruption of continuity molecular structure and percentage of

crystalline region in the urea fertilizers. In addition, the incorporation of chitosan at 1.5 wt% might contribute to the increase in crystalline region which contributes to the slower degradation rate of the samples. This is in good agreement with the soil degradation test results in Fig. 3.

### Fourier Transform Infrared (FTIR) Analysis

FTIR analysis was performed to verify the presence of urea in mixture comparing as-received urea with chitosan based urea fertilizer. The data evaluation was based on absorption bands concerned with the identification wave numbers of functional groups present in chitosan and urea. The bands wave numbers are tabulated in Table 4.<sup>17-20, 27</sup> From the spectrum of chitosan-urea blend in Fig. 6, possible -NH group stretching belongs to urea and chitosan were observed at  $3,450\text{ cm}^{-1}$  and  $3,361\text{ cm}^{-1}$ . Absorption bands at  $1,664\text{ cm}^{-1}$  and  $1,457\text{ cm}^{-1}$  indicates the presence of C=O in amide group and NH bending vibration in amide group. Furthermore, possible C-O group and -C-O-C- in glycosidic linkage of chitosan were observed at  $1,158\text{ cm}^{-1}$  and  $1,035\text{ cm}^{-1}$ , respectively.

**Table 3:** Melting temperature and percentage of enthalpy loss before and after degradation for chitosan based samples

Samples	Melting temperature, $T_m$ ( $^{\circ}\text{C}$ )		$\Delta H$ (J/g)
	Before	After	$\Delta H_{\text{Loss}}$ (%)
CBUF 1	138.14	134.43	85.44
CBUF 2	139.18	136.00	80.96
CBUF 3	137.79	134.85	84.61
CBUF 4	138.45	135.42	85.62
CBUF 5	137.50	134.54	83.31

**Table 4:** Identification functional groups for urea and chitosan based compound

Wavenumber	Functional Groups	Reference
$1667\text{ cm}^{-1}$	C=O Carbonyl band (amide group)	Osman and Arof (2002)
$1590\text{ cm}^{-1}$	NH <sub>2</sub> (amine group)	
$3450\text{ cm}^{-1}$	OH hydroxyl group	Pawlak and Mucha (2002)
$3450\text{ cm}^{-1}$ ; $3360\text{ cm}^{-1}$	NH group-stretching vibration	
$1660\text{ cm}^{-1}$	C=O in amide group	
$1560\text{ cm}^{-1}$	NH bending vibration in amide group	

1150 – 1040 $\text{cm}^{-1}$	C–O–C–in glycosidic linkage	Kadir, <i>et al.</i> (2010)
1660 $\text{cm}^{-1}$	C=O Carbonyl band (amide group)	
1591 $\text{cm}^{-1}$ to 1650 $\text{cm}^{-1}$ , 1557 $\text{cm}^{-1}$	NH <sub>2</sub> (amine group)	
3409 $\text{cm}^{-1}$	OH stretching vibration	Ibrahim, <i>et al.</i> (2010)
2921 $\text{cm}^{-1}$	CH stretching	
1954 $\text{cm}^{-1}$	NH <sub>2</sub> band	
1152 $\text{cm}^{-1}$ to 1033 $\text{cm}^{-1}$	C–O–C in glycosidic linkage	
2361 $\text{cm}^{-1}$	Primary amine group	Dhanakumar <i>et al.</i> (2007)
1640 $\text{cm}^{-1}$	C-O stretching of urea	Pritula, <i>et al.</i> (2007)
3450 $\text{cm}^{-1}$	NH <sub>2</sub> asymmetric stretching	

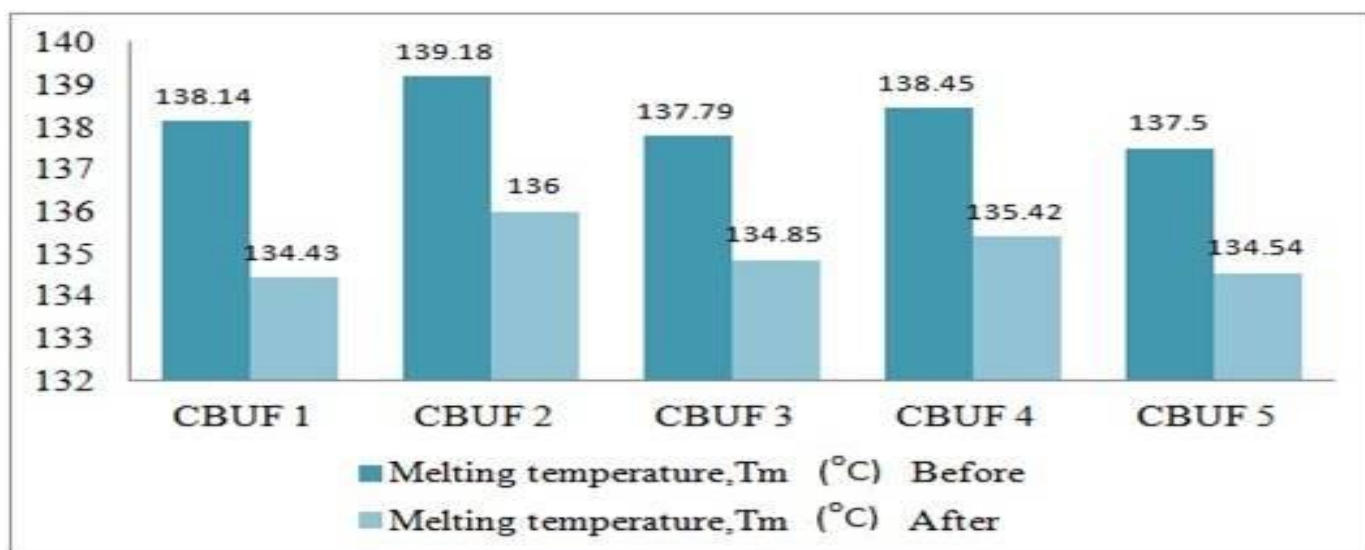


Figure 5: Melting Temperature T<sub>m</sub> before and after soil degradation



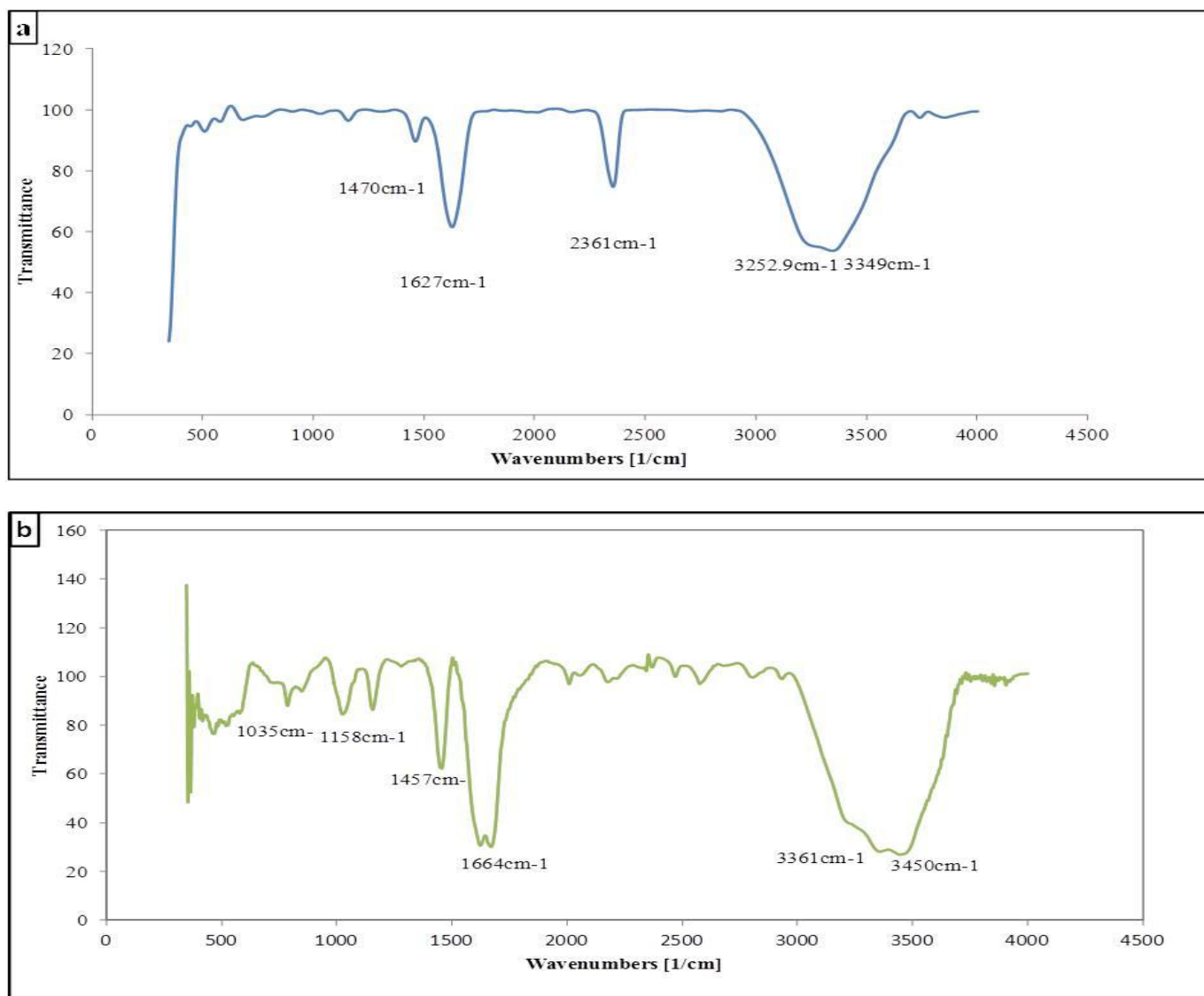


Figure 6: IR spectra of (a) as-received urea and (b) sample CBUF 3 (1wt% chitosan)

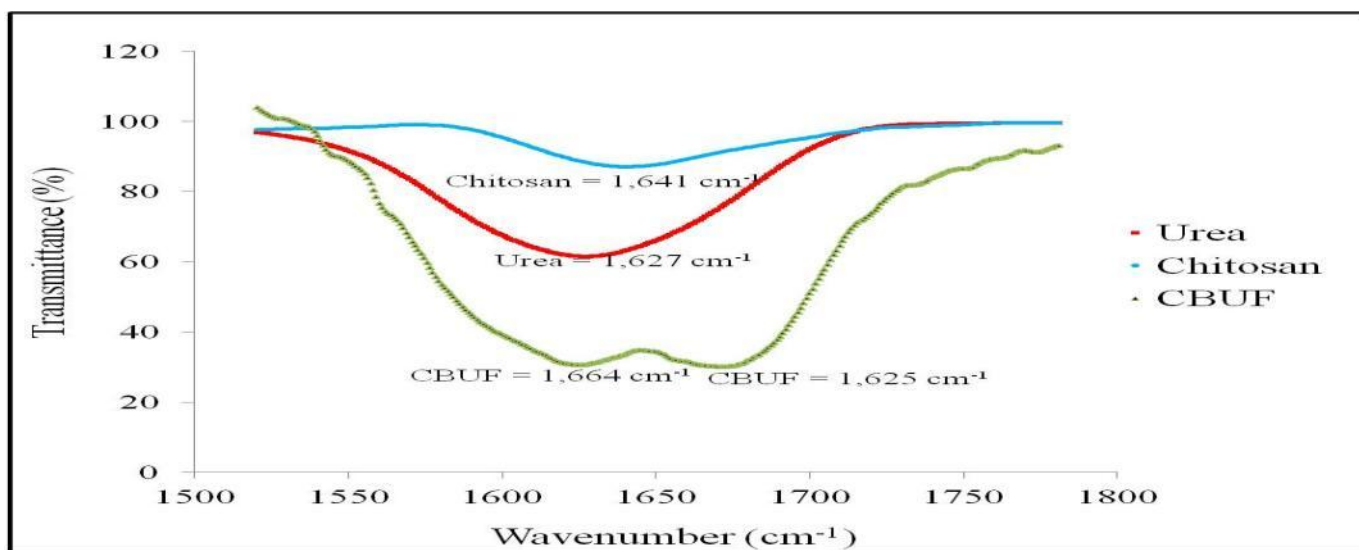


Figure 7: IR spectra of sample 3 chitosan based samples (1% of chitosan)



Further, FTIR spectra in Fig. 7 shows the comparison of critical absorption range between as-received urea, as-received chitosan and chitosan based fertilizer at 1 wt% chitosan. Within the range, it was found that stretching of C=O for amide groups were present at  $1,664\text{ cm}^{-1}$  and  $1,625\text{ cm}^{-1}$  for chitosan based sample. These might be due to the shift peaks in as-received urea and chitosan to new absorption band which resulted from homogenous urea and chitosan blend. Two peaks obtained in amide group of chitosan based samples were initially belongs to urea and chitosan at  $1,627\text{ cm}^{-1}$  and  $1,641\text{ cm}^{-1}$ , respectively. Both peaks were shifted to  $1,625\text{ cm}^{-1}$  and  $1,664\text{ cm}^{-1}$  in urea-chitosan sample. This analysis proved that there were good interactions between urea and chitosan when blended together in the sample.

### Conclusions

This study provides scientific understanding on the potential of chitosan as biodegradable binder in urea fertilizer. Overall, water absorption and weight loss percentage of produced urea fertilizers based chitosan were found directly proportional to the increasing chitosan contents which can be suggested might be due to the increase in hydrophilic properties. Significant difference in enthalpy before and after degradation confirmed that within 20 days, biodegradation has taken place to almost 80 % in the produced chitosan based fertilizers. Blend of chitosan and urea showed good interaction which evidenced from the amide groups in FTIR analyses. The shifted peak was observed at  $1,625\text{ cm}^{-1}$  and  $1,664\text{ cm}^{-1}$ . The optimum chitosan composition is critical to achieve the properties of slow release fertilizer where water absorption and degradation capability at their optimum rate. Thus, it can be concluded that chitosan has the potential to improve fertilizer's degradation rates in order to obtain slow-release properties but this may requires further investigation.

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