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Starch and polyvinyl alcohol encapsulated biodegradable nanocomposites for environment friendly slow release of urea fertilizer

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ABSTRACT

Low nitrogen (N) use efficiency from urea fertilizers due to environmental losses results in high cost of fertilizers for agricultural productions. Coating of urea with biodegradable polymers makes them effective for control and efficient N release. In this study, starch and polyvinyl alcohol (PVA) were used in combination with acrylic acid (AA), citric acid (CA) and maleic acid (MA) for the coating of urea prills. Different formulations of the coating were prepared and applied on urea prills such as urea coated with starch (10%) and PVA (5%) with acrylic acid: 2, 4 and 6% (USP-A2, USP-A4, USP-A6), with citric acid: 2, 4 and 6% (USP-C2, USP-C4, USP-C6), and with maleic acid: 2, 4 and 6% (USP-M2, USP-M4, USP-M6). After urea coating in fluidized bed coater, all uncoated and coated urea samples were characterized by scanning electron spectroscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), crushing strength and UV-Vis spectroscopy. The morphological and XRD analysis indicated that a new uniform coating with no new phase transformation occurred. Among all urea coated samples, USP-A2 and USP-C2 showed the highest crushing strengths: 12.08 and 13.67 N with nitrogen release efficiency of 70.10 and 50.74% respectively. All coated urea samples improved the spinach plants' foliage yield, chlorophyll content, N-uptake and apparent nitrogen recovery (ANR) than uncoated urea and control plants. However, USP-A2 and USP-C2 provided promising results among all coated samples with dry foliage yield (2208 ± 92 and 2428 ± 83 kg/ha), chlorophyll (34 ± 0.6 and 34 ± 0.4 mg/g), N-uptake (88 ± 4 and 95 ± 6 kg/ha) and ANR (59 ± 4 and 67 ± 6%). Therefore, urea prills coated with a combination of biodegradable polymers can be a better choice for the farmers to enhance agronomical productions by controlling the fertilizer nutrient release rate.

Introduction

The global food production and consumption demands are increasing with increasing population. To fulfil these demands, a large variety of synthetic fertilizers such as nitrogen (N), potassium (K) and phosphorus (P) fertilizers have been used for the enhanced crop production . Among all nutrients, N scarcity has remained a major issue affecting the plants' growth due to inability of plants to take up environment nitrogen [1]. Owing to this reason, urea remained the most commonly used nitrogen fertilizer during the past four decades [2]. Growers are compelled to use high rates of urea fertilizer that results in unintentional high losses, consequently polluting the agro-ecosystem. About 70% of N is lost into the environment that occurs due to ammonia volatilization, nitrification-denitrification, nitrate leaching and runoff [3].

Controlled releasing urea fertilizer will increase plant N use efficiency, reduce nitrate leaching and ensure constant nutrient supply to the roots relative to readily soluble fertilizer thus, improving nitrogen recovery [4,5]. Various type of controlled-releasing fertilizers have been used previously such as; encapsulated soluble fertilizers, inorganic salts or decomposable organic compounds with low solubility, readily decomposable water soluble materials and less soluble chemical materials bio-augmented with bacteria [6,7]. From all those, encapsulated fertilizers proved best due to their slow releasing nature and less solubility effect. Also, urea encapsulation could be a good management strategy

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to increase its plant fertilizer value and to solve the problem of N losses [8].

Polymeric substances obtained from plastic or petroleum products have been extensively used during the last few decades as coatings for the formation of controlled/slow releasing fertilizer. The polystyrene, polylactic acid [9], polysulfone, polyurethane [10] and polyacrylamide [11] materials have been employed as coating materials for urea to make them slow releasing fertilizers [12,13]. However, these substances have high cost and show poor biodegradability that means they persist in the soil for a long time and disturb the soil quality. Therefore, there is a need to use biodegradable materials for coating urea prills that will eliminate the harmful effects of conventional coating on agro-ecosystems. To avoid the harmful impacts of non-biodegradable coating materials on the environment, researchers started using bio-based coatings such as molasses, gum, starch, polyurethane and honeybee wax [14]. Many recent studies have used the coatings of natural biomasses such as rice straw and rice husk, lignin, cellulose, chitosan either alone or mixed with other minerals [3,15,16]. Irfan et al, [17] evaluated the effect of these bio-based materials on the zinc release efficiency of urea fertilizers.

Due to complete biodegradability, renewability and low cost, starch proved to be a capable candidate for coating thus, producing valuable materials. However, due to its poor processability, dimensional stability, mechanical properties and instability at higher temperature and pH, it cannot be used directly. Starch blends with polyurethane and polysulfone have been employed but the problem was to minimize the ratio of synthetic polymers into natural bio-polymers to achieve the desired biodegradability of coated urea in the soil [18]. The polyvinyl alcohol (PVA) which is a water-soluble synthetic and biodegradable polymer, was selected to enhance the mechanical properties of starch/PVA blends [19,20]. Strong interaction and crosslinking in PVA-starch blends not only increase the strength and density of films but also prevent swelling of the starch structure by decreasing accessible regions, thus resulting in improved resistance to dissolution [21].

Various methods including rotary pan coating, rotary disk atomization, immersion technique [9] and fluidized bed coating (FBC) have been employed for the production of coated urea fertilizers. However, the FBC technique is considered the best among all other techniques due to its excellent heat and mass transfer characteristics, short processing time and single operating unit [22]. In fluidized bed coater, the granulation process strongly depends upon the nature and quantity of binders/cross linkers [23]. The osmotic pressure builds inside the coating when urea coated fertilizers come in contact with water. If osmotic pressure increases from threshold pressure, the weakly bonded coating breaks and releases all fertilizer which is referred as “failure mechanism” [24].

Wu et al, [19] suggested that the addition of some binders or cross linkers into the PVA-starch blends provides the coating material with more flexibility, strength and water resistibility. Shaaban et al, [25] used boric acid as a binder for urea encapsulation and found that the boric acid slowed down the nitrogen release rate of urea by increasing its crushing strength. Different biodegradable binders such as bentonite clay for urea-zeolite fertilizer, paraffin wax into the gypsum and sulphur coating of urea fertilizers have been used for increasing the nitrogen release efficiency [26–28]. Moreover, Sofyane et al, [18] studied the nutrient release rate from PVA/starch based coated urea using glycerine as a binder/cross linker. In few recent studies, the use of carboxylic acid such as acrylic acid has been employed as a cross linker [12,19,21,29] but there is a lack of literature regarding the real field applications of synthesised encapsulated urea as well as the effect of changing the amount of acid (plasticizer) on the nutrient release efficiency.

To the best of our knowledge, only limited studies compared the release rate efficiency of urea fertilizers by using carboxylic acids as cross linkers with an appropriate combination of PVA and starch and applied them on plants. Therefore, this study aims to develop novel coated urea and then to evaluate their N-releasing efficiency in real field applications. For this purpose, three different carboxylic acids such as acrylic acid, citric acid and maleic acid were selected as cross linkers to encapsulate urea prills. These carboxylic acids in different weight percentages (2-6%) were added to PVA and starch solutions to form novel coating formulations and coated on urea prills in fluidized bed coater (FBC). The coated urea samples were also compared with uncoated urea for N release rate and plants N uptake enhancement in field-scale experimentation. The prepared samples were subjected to the SEM, FTIR, XRD, crushing strength testing and UV-visible spectroscopy for the urea release measurements. Moreover, the prepared coated fertilizers were applied to the spinach plants to evaluate their impact on plant yield, chlorophyll content and N-uptake measurements.

Table 1
The treatments and chemical compositions of coating solutions for urea encapsulation in wt%.

Treatment	Starch	PVA	Acrylic Acid	Citric Acid	Maleic Acid
USP-A2	10	5	2	-	-
USP-A4	10	5	4	-	-
USP-A6	10	5	6	-	-
USP-C2	10	5	-	2	-
USP-C4	10	5	-	4	-
USP-C6	10	5	-	6	-
USP-M2	10	5	-	-	2
USP-M4	10	5	-	-	4
USP-M6	10	5	-	-	6

Note: USP-A2 to A6: urea coated with starch, PVA and acrylic acid (2, 4, 6 %); USP-C2 to C6: urea coated with starch, PVA and citric acid (2,4,6%); USP-M2 to M6: urea coated with starch, PVA and maleic acid (2,4,6%).

Materials and methods

Materials

Starch, PVA, maleic acid, citric acid, acetic acid, P-dimethyl amino benzaldehyde and concentrated HCl were purchased from Dae Jung Co., Korea. Distilled water was used as a solvent. Sieved urea prills of 2 mm diameter having 46% N were obtained from a local market (Fauji fertilizer bin Qasim Company, Pakistan). All chemicals were commercially available in analytical grade and used without any purification.

Preparation of coated urea samples

The coated urea samples are prepared by using the previously reported method with some modifications [22]. The chemicals used along with their quantities to prepare coating solutions are presented in Table 1. The coating materials, as well as their concentrations, were selected by keeping in view the previous literature [12,20,29,30]. The starch solution (10%) was prepared and plasticizers were added to it. Then PVA (5%) was added to the starch solution which was prepared in distilled water after heating at 98°C and stirring for 45 min. Here, acrylic acid, citric acid and maleic acid cross linkers are used to make starch and PVA better compatible with each other due to the hydroxyl functional group presence in both [19].

Then the prepared coating solution was stirred continously for 20 min at 40°C on a heating plate to homogenize coating solution. After preparation of coating formulations, the urea prills were coated using a mini spray granulator YC-1000 (Shanghai Instrument & Equipment Co., Ltd.). For each batch/experiment, 200 gm of urea prills was fed into the feed section of the fluidized bed coater and coating material was introduced from the bottom of the fluidizer. Then the air was blown through the heater at 80°C with 45 Hz blower frequency in constant 0.2 MPa air pressure to fluidize the prills and coating solution was pumped into the fluidizer with 30 rpm speed. The whole procedure was followed for 30 min and prepared coated urea samples were taken out of the bed and dried for 15 min [22].

Table 2
Physiochemical properties of soil subjected to plants growth.

Soil properties	Values
Soil texture	Clay loam
pH	8.40
EC (dS/m)	0.21
Total organic carbon (%)	0.16
Dissolved organic carbon (mg/kg)	3.40
Mineral nitrogen (mg/kg)	4.60

Characterization of coated urea

SEM (S-4700 Hitachi, Japan) was employed for the morphological study of coated and uncoated urea prills [31]. FTIR was done with Perkin Elmer Spectrum 100 spectrometer, wavenumber ranging from 400 to 4000 cm^{-1} to analyse the presence of bonds, functional groups and required crosslinking. To check the crystallinity of synthesized formulations, XRD analysis of coated and uncoated urea were performed with STOE Germany [32]. The crushing strength of uncoated and coated urea fertilizers was also evaluated. Crushing strength is the required force to crush the particle. It is the measure of the resistance of the coating to fracture during physical handling throughout the supply chain [33]. A universal testing machine (AGX Plus) is used for this purpose that tells about the tensile strength and compressive strength of materials. Usually, uncoated urea prills get easily break down into powder due to their delicate nature that further remains of no use in agriculture. Urea prills were placed under metal plunger of the machine and tested against a calculated amount of stress. Stress at which urea prills cracked was marked as the measure of their tensile strength [30].

Determination of urea release rate

The urea release rate and efficiency of the release of coated/uncoated urea prills were determined by using p-methyl amino benzaldehyde method [33]. The absorption of the sample was measured with UV-Vis spectrophotometer (GENESYS^{TM} 20). The calibration curve was drawn to obtain the slope values by plotting graphs between the known concentration of urea versus absorbance to check the urea release rate. Stock solution was prepared by dissolving 10 gm of urea samples into 5 L deionized water in a beaker. At different time intervals (3-120 min), the sample aliquots (10 mL) were taken from the stock solution, diluted to 50 mL and mixed with 1 mL HCl and 5 mL P-dimethyl amino benzaldehyde solution in 50 mL volumetric flask. Finally, the absorbance of the prepared solution was measured at the wavelength of 418 nm to obtain the unknown urea concentration in solution or urea release rate by using Eq. (1), and efficiency by using Eq. (2) [34].

$$\text{Urea (ppm)} = \frac{\text{Absorbance} - \text{Y intercept}}{\text{Slope from calibration curve}} \tag{1}$$

$$\text{Efficiency (\%)} = \frac{C_u - C_{cu}}{C_u} \times 100 \tag{2}$$

where, C_{CU} and C_U represent the urea concentration (ppm) in coated and uncoated urea sample solutions at the time interval of 9 min respectively.

Pot experiment

For pot experiment, the top soil was collected from the research field and sieved to pass mesh (2 mm) to remove all non-soil particles such as debris and gravels etc. The soil was analysed before applying any treatment and soil properties are presented in Table 2. The soil properties such as total carbon and nitrogen contents were determined and excluded from the obtained values of results after urea application for more precision. After sieving, each earthen pot (30 cm diameter) was filled with 4 kg of soil and spinach seeds were sown in them. In total 11 treatments were randomly allocated in 44 pots with four replications in a complete randomized design (CRD).

The treatments were (1) control/untreated (C) plants without any urea application, (2) uncoated urea (UC), and other 9 treatments of coated urea as already presented in Table 1. The urea prills were applied in four splits; before sowing seeds and after 1st, 2nd and 3rd harvesting of spinach plants. Phosphorous and potassium fertilizers (75:100 kg/ha) were applied through their sources such as triple superphosphate and muriate of potash respectively. To provide the plants with natural conditions, pots were placed in the open air and irrigated regularly to maintain soil water holding capacity (60%) measured through a low-cost moisture meter (FY-901, Hangzhou FCJ I and E Co., Ltd, China) [30].

Plant sampling and analysis

The foliage of spinach crop was harvested at ground level by using a sharp knife four times at 60, 90, 150 and 180 days after sowing and fresh foliage yield was recorded for each treatment. Chlorophyll content of fresh leaves from each pot was measured by using SPAD chlorophyll meter. Afterwards, each treatment plant sample was dried in an oven at 70 °C for 48 hours until weight became constant to obtain dry foliage yield. Each dried sample was ground and analysed for total N content using Kjeldahl digestion method [35]. Foliage N uptake was calculated by using Eq. (3) while apparent nitrogen recovery (ANR) through Eq. (4).

$$\text{FNU} = \text{NC} \times \text{DFY} \tag{3}$$

$$\text{ANR (\%)} = \frac{(\text{NC}_{\text{treated}} \times \text{DFY}_{\text{treated}}) - (\text{NC}_{\text{control}} \times \text{DFY}_{\text{control}})}{\text{NA}} \tag{4}$$

where FNU, NC and DFY represent foliage N uptake (kg/ha), nitrogen content (gm/100 gm dry matter) and plant dry foliage yield (kg/ha) respectively. NA is the total nitrogen (N) application rate per treatment (kg/ha).

Statistical analysis

Univariate analysis was done to evaluate treatment effect with SPSS statistics version 20 (IBM, NY, USA). The effect of coated and uncoated fertilizers was analysed using analysis of variance (ANOVA) at a probability level of 5%. When the effect of treatments proved significant then Tukey test was used for multiple comparisons [35].

Results and discussion

Microstructure characteristics of coated urea prills

The SEM micrographs of all uncoated and coated urea samples are shown in Fig. 1. The surface micrograph of uncoated urea prills in Fig. 1 (a) shows the fine pointy crystals that are tightly cemented on to the surface. Some of the gaps and pores are also visible. Since onion rings are illustrated to appear during urea production theoretically [36]. Unfortunately, ring formation is not clearly visible here and the surface looked rough with clear pointy crystals. SEM micrographs of coated urea show layering and agglomeration that is a clear indication of the coating. In Fig. 1 (b1), SEM micrographs of USP-A2 are shown which represent that only a few slabs are present with pointy edgy particles on the surface.

This coating is covering the whole surface without any gaps and cavities that indicate the good coverage of urea prills. Here the coating is quite dense without the pointy exposed surface of urea through gaps and agglomeration occurs due to thorough contact between urea surface and coating [37]. With the increase in the percentage of AA (4 %) in USP-A4 samples, the random bigger slabs with some eddy particles

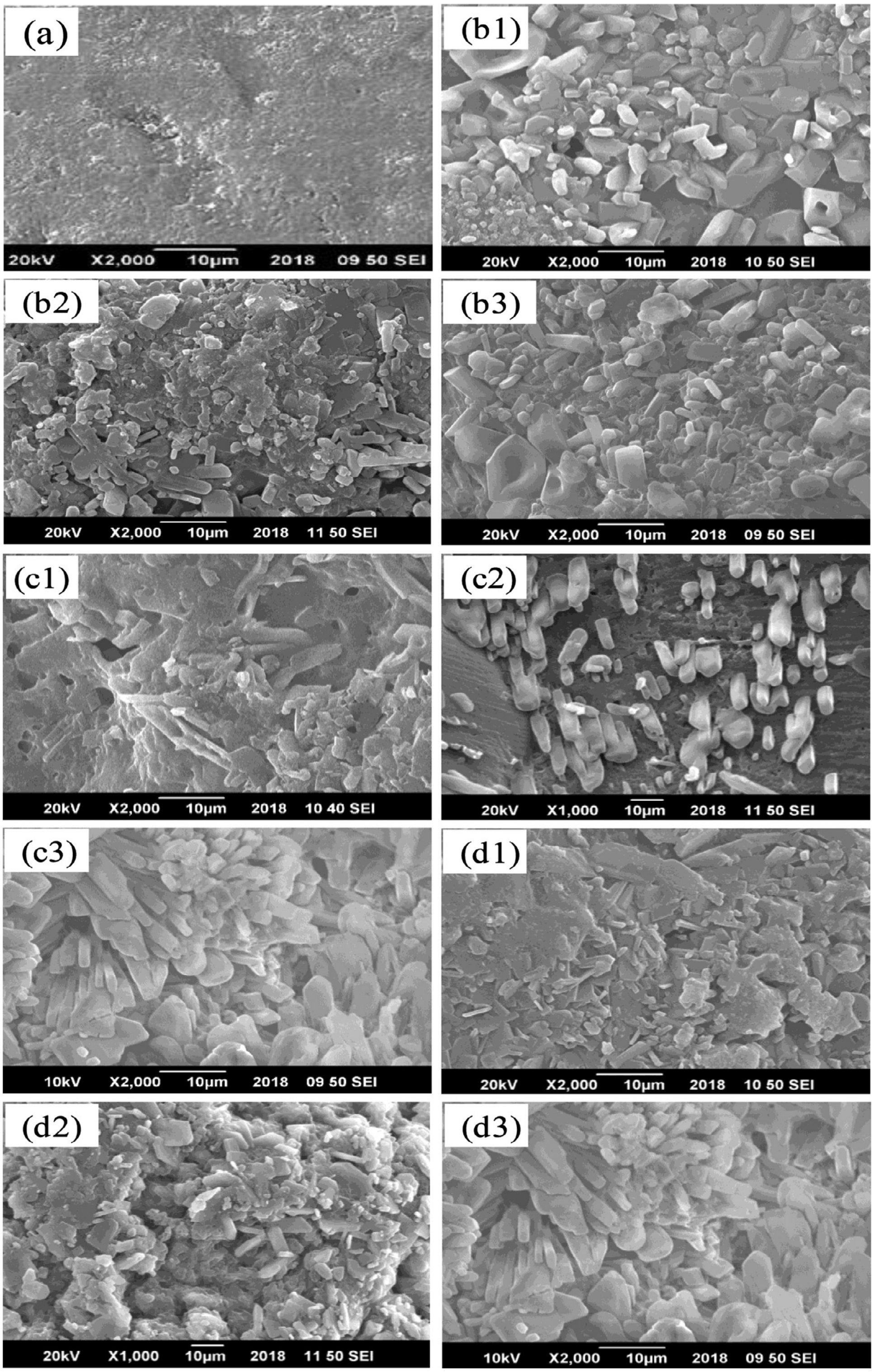

Fig. 1. SEM images; (a) uncoated urea, (b1, b2, b3) USP-A2 to USP-A6, (c1, c2, c3) USP-C2 to USP-C6 and (d1, d2, d3) USP-M2 to USP-M6.

appeared and the coating layer seem to be dense with some pores and cavities. Few areas are best covered and dense but some of the portions are edgy which indicate the appearance of the urea surface (Fig. 1 (b2)).

As the urea surface is visible that means coating at that region is not intact with the surface and urea prills were uncovered at those places as also reported in previous literature [38]. Relative to USP-A4, USP-A6 in Fig. 1 (b3) is showing a surface with pointy edges leading to the urea surface appearance through pores along with a small random region of compact and intact covering. This shows that with an increase in the concentration of cross linkers (acids) in the coating formulations from 4 to 6%, the cracks start to propagate on to the coating surface that exposes urea under coating. Azeem et al, [22] also stated that an optimum concentration of coating materials plays a crucial role in the nutrient release rate.

The SEM micrographs of urea coated with starch, PVA and citric acid (USP-C) show dense, homogenous, smooth and continuous surface without the appearance of any pores. The white granules are maybe the starch granules, and they can reduce the mechanical properties due to their brittle behaviour [19]. In Fig. 1 (c1) no projections and wrinkles are visible which is an indication of no significant phase separation between the starch and PVA in USP-C2 samples [39]. It also indicates that citric acid acts as a bridge and enhances the binding of starch and PVA and helps in forming a dense and homogenous film. Lower concentrations of citric acid (in USP-C2) show surface morphology of smooth and fully dispersed coating.

By increasing the concentration of citric acid (4%) in USP-C4 sample, the agglomeration on the surface of the urea prill also increases (Fig. 1 (c2)). As the concentration of citric acid is increased that contribute to the chemical networking between coating components at a higher rate, without providing enough time to the coating film to spread evenly on the urea prills' surface. And the projections due to citric acid and pores due to agglomeration start appearing at this point and the gaps appeared to expose the urea surface. However, with a further increase in the concentration of citric acid (6%) in USP-C6 sample, the projections become more prominent. And the edges appear due to the exposed surface of urea through gaps, cavities or imperfections in the coating as shown in Fig. 1(c3). Thus, among all the coatings including citric acid, the sample USP-C2 has shown dense and complete coverage of urea prill. Moreover, the absence of edgy pointy particles is the major indication of good coverage [40].

The SEM micrographs of urea coated with starch and PVA with maleic acid (USP-M) are shown in Fig. 1 (d1). With a lower concentration of maleic acid (2%) in USP-M2, the surface of the urea is partially covered with coating. However, some of the regions are showing spikes or edges on the urea surface that is the representation of incomplete coverage due to pores and cavities. While an increase in the concentration of maleic acid (4%) in USP-M4, appears to fill the gaps and crevasses (Fig. 1 (d2)). This forms dense clusters of particles on the urea surface due to thorough contact with coating, surprising the appearance of urea surface. Xiaolong et al, [24] stated that this intact coating will prevent and control the urea release rate better.

With an increase in the amount of maleic acid (6%), the intact behaviour of coating with the urea surface reduces (Fig. 1 (d3)). Plasticizer gets agglomerate creating big holes and cracks in coating causing urea surface to appear. These cracks will show the edgy particles indicating the uncoated region that affects the release rate badly. Moreover, the combinations of coating materials that caused agglomeration and cracks on the urea surface appeared to be more crystalline due to the non-homogenous type of coatings. It can be observed from the above discussion that the coated samples USP-A2, USP-C2 and USP-M4 showed the best-covering properties. Their surface appeared to be smooth, homogenous, continuous and dense with no visible pores. It indicates that carboxylic acid crosslinkers (acrylic acid, citric acid and maleic acid) improves the binding of starch and PVA. Furthermore, the poly-carboxylation reaction between plasticizers and hydroxyl groups of PVA/starch provide support to the uniform nature of the coating. By combining the PVA and starch hydroxyl groups, plasticizers enhance the water resistibility of starch films by suppressing their hydrophilic nature. Thus, all the plasticizers were cross-linked with starch and PVA and well dispersed [19]. The rough outer layer in the coated sample also prevents the mechanical damage of coating and enhances the water retention capability in the soil [12].

Interaction of urea with coating formulations

FTIR spectra of uncoated and coated urea samples were recorded at an ambient temperature of 25 °C and wavelength of 400–4000 cm^{-1} and shown in Fig. 2. In the FTIR band of uncoated urea powder, the bond of primary amine was observed that represents the N-H stretching in urea. This band is comprised of two peaks first is at 3442 cm^{-1} and another at 3348 cm^{-1}. Two more bands of high intensity appear, one at 1677 cm^{-1} corresponds to the C=O [41] and another 1624 cm^{-1} for vibrational stretching of N-H bond [42]. A band of the slightly low intensity of 1468 cm^{-1} was also observed that corresponds to the vibrational stretching of the C-N bond in urea. These absorption peaks are consistent with relatively published results [43,44].

The characteristic N-H band in urea starts disappearing in the case of covering of urea with coating. The slight band shift in carbonyl was also seen which is the indication of strong interaction through hydrogen bonding between the carboxyl group of urea and hydroxyl group of starch. The FTIR spectrum shows that with increasing concentration of plasticizers by keeping polymer ratio same the coating and hence bonding becomes strong, this was also visualized by greater agglomeration in SEM analysis (Fig. 1). This was verified by the absence of a primary amine band in the spectrum and decreased intensity of C=O and C-N bands in urea. In the fingerprint region (400-1500 cm^{-1}) all the usual peaks of uncoated and coated urea samples appear very similar.

The FTIR spectrum of urea coated with starch, PVA and acrylic acid is shown in Fig. 2 (a). The characteristic peaks of the amine bond ($-NH_2$) changed slightly in USP-A2, giving two bands in the regions of 3400-3300 cm^{-1} and 3330-3250 cm^{-1} respectively [39]. The C-N stretch at 1468 cm^{-1} for urea, is shifted due to crosslinking of urea with starch, PVA and acrylic acid. The band at 1147 cm^{-1} is crystallinity dependent and is characteristic for PVA [45]. It appears in USP-A2 and is weakened with the increase in the concentration of acrylic acid. It might be due to the deformation of the structure of PVA after crosslinking.

With the addition of acrylic acid which is a carboxylic acid, it shows a strong broadband of O-H in the region 3300-2500 cm^{-1} [46]. However, due to crosslinking of starch and PVA with the carboxylic acid, the amine band becomes less sharp which is indicating the homogenous coating of urea, exposing fewer N-H groups. The decrease in sharpness and broadening of the band is an indication of hydrogen bonding between the carbonyl bond of starch and OH of PVA [44]. The reason for the broad O-H stretch band is that carboxylic acids usually exist as hydrogen-bonded dimers. Carbonyl (C=O) stretching is also seen in the region of 1760-1665 cm^{-1} and in Fig. 2 (a) it is indicated at 1677 cm^{-1} [47,48]. With the addition of carboxylic acid, it gets broadened which indicates the increasing concentration of acrylic acid.

In Fig. 2 (b), the spectrum for uncoated urea contains primary amine with N-H symmetric and asymmetric stretch in the region of 3400- 3250 cm^{-1}. The decrease in intensity from 3200-3500 cm^{-1} after cross-linking with citric acid is ascribed due to the hydroxyl groups. This decrease and broadening of peaks are increasing with increasing citric acid content of the mixture [49]. A new peak at 1619 cm^{-1} indicates the formation of –C=C– structure in PVA chains [39]. O-H band at 1444.5 cm^{-1} of carboxylic acid can be seen in USP-C6. The band appearing at 1781 cm^{-1} correspond to ester carbonyl and carboxyl bands in USP-C4 [50]. The ester carbonyl, carboxylic and C=C bond formation justify the good interaction among starch, PVA and citric acid presenting it to be a suitable coating formulation for urea.

Fig. 2(c) shows the spectrum of urea coated with starch, PVA and maleic acid blend. There is no new bond appeared in the spectrum but the bonds C=O and C-O in uncoated urea get broadened after coating. This broadening of bonds is due to crosslinking between the carboxyl groups of maleic acid and -OH present in starch or PVA due to hydrogen bonding which cover the existing C=O and C-O bonds in uncoated urea (UC) [39]. So the maleic acid is proved to be a good binding agent for PVA and starch on urea. In USP-M2, the peaks are almost the same as for uncoated urea. However, due to crosslinking of starch and PVA with the carboxylic acid, the amine band becomes less sharp. The decrease in sharpness and broadening of a band is an indication of hydrogen bonding between the C=O bond of starch and OH bond of PVA [39].

Crystalline behaviour of coated urea

The crystal structures of uncoated and coated urea samples explained by XRD analysis at a scan angle of 2θ =20 to 60° is presented in Fig. 3. Along with urea peaks, the effect of cross linkers on the PVA and starch coating structure can also be investigated by XRD [12]. Uncoated urea shows characteristic peaks at 22.5°, 24.7°, 31.9°, 37.5° and 45.6°. Starch

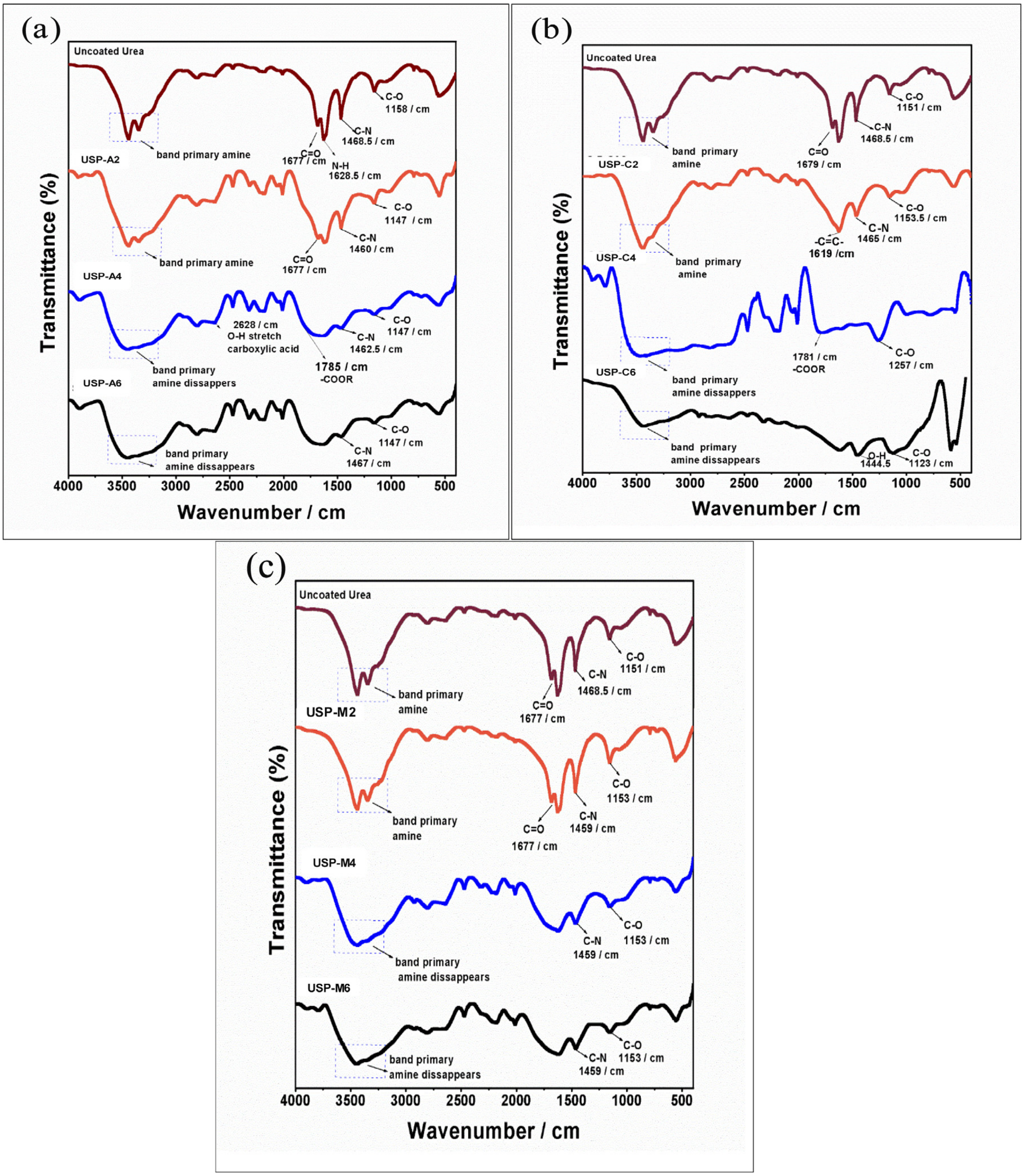

Fig. 2. FTIR analysis of urea coated with starch, PVA and (a) acrylic acid: USP-A2 to USP-A6 (b) citric acid: USP-C2 to USP-C6 and (c) maleic acid: USP-M2 to USP-M6.

shows a peak at 35.7°, PVA shows a peak at 19.2°, acrylic acid at 29.5°, maleic acid at 31.9°, citric acid at 31.7° and 44.9°. The absence of PVA peak in XRD spectrum is an indication of the destruction of crystalline structure with an increase in amorphous nature. Some of the peaks reorient due to crosslinking, resulting in higher crystallinity [51] such as peaks of AA and starch in the case of USP-A samples. An increase in peaks intensity shows improved crystallinity due to increased crosslinking.

The lowest intensity of urea peaks was observed at the optimum concentration of cross linkers, supporting a well-homogenized coating. The greater number of higher intensity peaks of coating components (PVA, starch, AA, CA or MA) appear due to an increase in the concentration of cross linkers in USP-A and USP-C samples. Starch is a semi-crystalline in nature and its peak also disappeared in many of the coatings due to deformation of its structure as in USP-A2 and USP-C2 (Fig. 3 (b1), (c1)). Azeem et al, [12] proved that citric acid enhances the binding of PVA with starch by O-H bonding, thus reduces the crystallinity of coated urea and support the homogenous coating.

USP-M2 is showing peaks of higher intensity but with an increase in the concentration of maleic acid in USP-M4 and USP-M6 samples, the obtained peaks are not as high, which is due to restriction of chains with further increase in maleic acid (Fig. 3 (d2), (d3)). In the case of maleic acid, the double-helical structure forms due to hydrogen bonding but when OH bonds get substituted by ester bonds, the double-helical structure changes. These changes destroy the crystalline/semi-crystalline structure and lower the relative crystallinity [52, 53]. As no new peaks or very low new peaks were seen in the coated urea prills, it may be said that no new phases were formed or no deformation in the

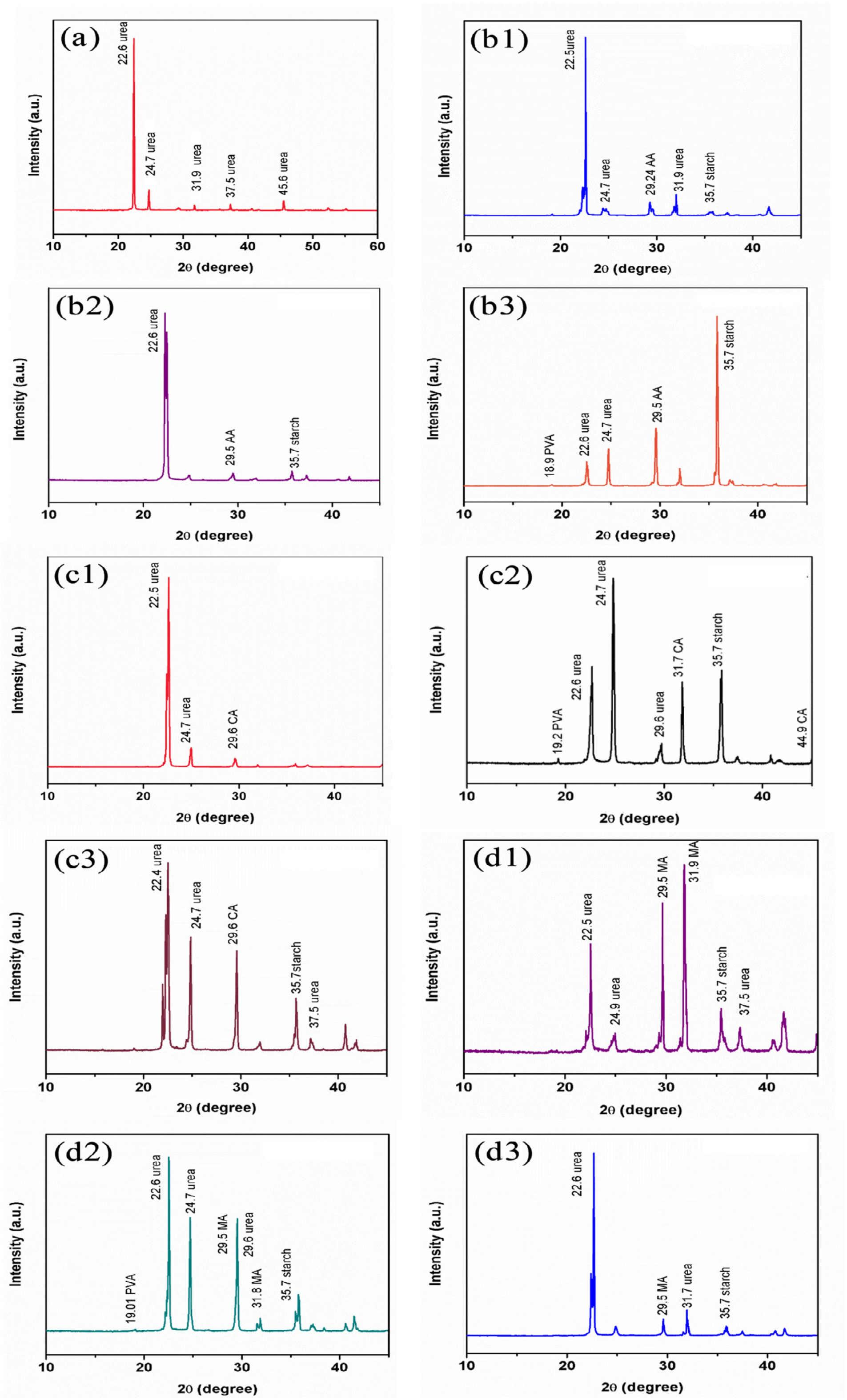

Fig. 3. X-ray diffraction analysis; (a) uncoated urea and urea coated with starch, PVA and (b1-b3) acrylic acid 2-6% (c1-c3) citric acid 2-6% and (d1-d3) maleic acid 2-6%.

structure took place during the coating process indicating the coating formulations to be successful for urea [54,55].

Crushing strength of coated urea

Crushing strength is determined by applying pressure to specified size urea prills until they fracture [56]. To find crushing strength equal size of prills must be analyzed as with the increase in size, crushing strength also varies [33]. The crushing strength greatly depends on the chemical composition of the coating. An increase in crushing strength indicates the physical barrier that retards water. Water absorption has a negative effect on coated prills as it disintegrates the prills, forming them sticky and releases the nutrient content [34].

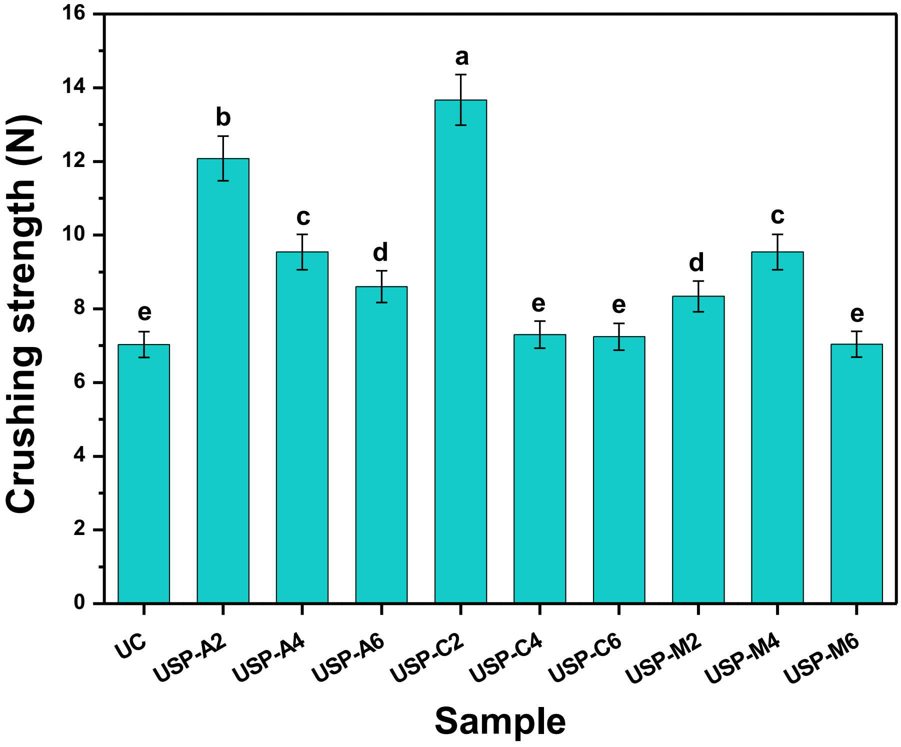

Fig 4. Crushing strength of uncoated and coated urea samples. Letters on the bars indicate the differences among treatments at 5% level probability. Error bars show standard error of the mean (n=4).

From Fig 4, it can be seen that all type of coated urea showed higher crushing strengths than uncoated urea (7.01 N). In the case of acrylic acid crosslinkers, the highest crushing strength was observed in the case of USP-A2 (12.08 N) and with the increase in acrylic acid concentration, the ability of USP-A4 and USP-A6 to resist against external strength decreased to 9.54 and 8.60 N respectively. Similarly, in the case of citric acid crosslinker, USP-C2 showed 13.67 N crushing strength which decreased in USP-C4 (7.30 N) and USP-C6 (7.24 N) by increasing acid concentration. While in the case of maliec acid crosslinker, a slight increase in crushing strength occurred from USP-M2 (8.34 N) to USP-M4 (9.54 N) after which it decreased again in USP-M6 (7.04 N).

It can be observed from Fig 4 that the minimum acid percentage in the coating, based on acrylic acid and citric acid provided good coverage leading to good crushing strength. The coverage properties of coating materials have also been presented in SEM analysis (Fig. 1) of coated urea which is in agreement with the crushing strength of particles. Higher acid concentration leads to greater cross-linking, restricting chain mobility and hence decreasing tensile strength [57]. This can also be due to good dispersion between polymers and plasticizers such as in the case of maleic acid crosslinker. Although the increase in acid concentration enhanced crosslinking between starch and PVA. Unfortunately, over-crosslinking showed agglomeration that resulted in the appearance of cracks on the coating surface.

Thus, an increase in the acid concentration in coating material lead to higher stiffness, crystallinity, brittleness and immobility resulting in the decreased flexibility which in return, made the coating prone to damage easily [58]. It is clear from Fig 4 that increase in concentration of plasticizers does not result in good crushing strength and compatibility. This decrease in crushing strength may be due to the restriction in the movement of polymer chains. Mikhailova et al, [59] stated that increased concentration of plasticizers restricts the movement of the polymeric chains. Hence, the flexibility of the coating decreases and then mechanical strength. Less flexibility and strength may induce cracks in the coating during handling and transportation. Naz and Sulaiman [60,61] observed the 8% increase in crushing strength of urea after coating with a 0.7 mm thin film of modified starch polymer.

Release rate of coated urea

When coated and uncoated urea is immersed in water it gets dissolve either by catastrophic or diffusion mechanism [62]. And nutrient release occurs from urea in three main steps: The initial stage of the lag period during which negligible release is observed, second is the constant release stage and the last stage during which a gradual reduction in release rate occurs, called the mature stage [63]. The amount of urea release from uncoated and coated urea samples was determined as a function of time at 25 °C by using Eq. (1) and the results are presented in Table 3. The release mechanism starts when water vapours penetrate through the coating and dissolve the fertilizer core due to an increase in internal osmotic pressure [5]. The release of nitrogen from conventional uncoated fertilizer was very fast and all nitrogen was released from uncoated urea within 3 min (Table 3). This is an actual and usual trend of nitrogen release from nitrogenous fertilizers without any coating (uncoated urea prills) [64].

As there is no physical barrier to the fertilizer water dissolves it immediately. The catastrophic release can be seen at this point. No gradual or lag period is demonstrated by fertilizer due to the absence of any physical barrier [65]. All coated urea samples show a slow release of nitrogen from urea prills as compared to the uncoated urea prills. From Table 3, it can be seen that USP-A2 sample showed urea dissolution of 13.50-15.75 ppm from 3-6 min by diffusion mechanism in a lag stage. Then from 6 to 12 min, the gradual release mechanism was observed in which water penetrates through diffusion and nitrogen releases slowly from inside of the coating to the outer surface. From 12 min to onwards, mature release starts in which water penetrates through fissures on coating and develops high pressure with the gradual release (80 ppm) of nitrogen through the polymeric coating.

After 12 min total urea is dissolved (all N released) into the water and become invisible. The 80 ppm concentration of the solution is considered complete urea release from all uncoated/coated urea samples. While in the case of USP-A4, the urea release start from 3 min with a gradual release rate (21.90 ppm). However, from 12 min to onwards, all urea released completely (80 ppm) and dissolved in water.

Table 3
The concentration of urea release from uncoated and coated urea prills in the water at different time intervals and 25°C.

Time (Min)	Concentration of urea sample solutions (ppm)									
	UC	USP-A2	USP-A4	USP-A6	USP-C2	USP-C4	USP-C6	USP-M2	USP-M4	USP-M6
3	72.75	13.50	21.90	60.25	17.75	13.58	6.08	29.41	2.75	33.43
6	80	15.75	44.41	68.58	28.58	32.75	36.91	49.41	52.75	51.08
9	80	23.92	72.75	80	39.41	68.58	80	75.34	77.12	78.50
12	80	80	80	80	61.90	80	80	80	80	80
15	80	80	80	80	62.75	80	80	80	80	80
30	80	80	80	80	80	80	80	80	80	80
60	80	80	80	80	80	80	80	80	80	80
120	80	80	80	80	80	80	80	80	80	80

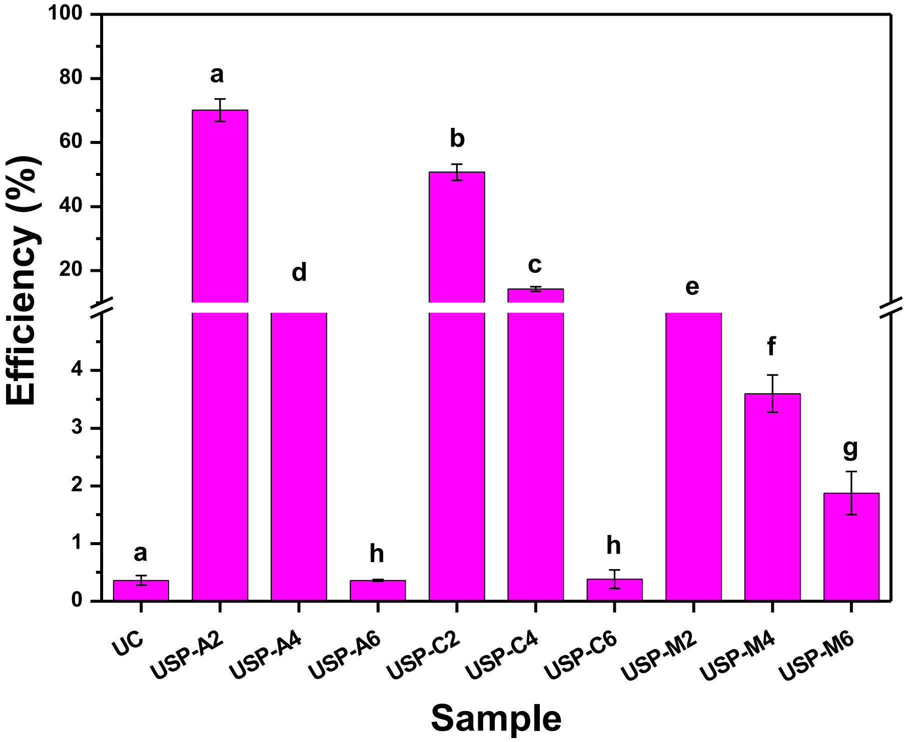

Fig. 5. Urea release efficiency of uncoated and coated urea samples. Letters on the bars indicate the differences among treatments at 5% level probability. Error bars show standard error of the mean (n=4).

The urea releases at this stage with a constant diffusion rate so this stage is called a mature stage. The USP-A6 sample showed that all urea released at 9 min in the mature stage. The release concentration (60.25 ppm) of USP-A6 is higher than USP-A4 (21.90 ppm) at the first 3 min of reaction therefore, USP-A6 releases earlier before 9 min than USP-A4 sample.

It can be deduced here that with the increase in plasticizer (AA) concentration, the release rate is getting higher. The reason is the restriction in polymeric chains with more plasticizer. This will make the coating less flexible and fragile causing the cracking of the coating as it was also observed through SEM analysis (Fig. 1) and cracks lead to the early release of fertilizer [66]. According to Bilal et al, [34] the release of urea from inside the coating depends largely upon the homogeneity of coating over urea prills and the strength of chemical binding forces of coating materials among themselves and with urea.

The USP-C2 sample shows a gradual release of 17.75 to 61.90 ppm (during 3-12 min) leading to the lag stage (12-15 min) and gradual release stage of 62.75 to 80 ppm again (from 15 to 30 min). Finally, after 30 min all urea has released in the mature stage. This huge time-lapse shows that this coating retards the release of urea from the urea sample better than all previous coatings. Similarly, USP-C4 showed 3 to 12 min gradual release followed by 12 to 15 min of the lag period, after which release rate (80 ppm) became constant for USP-C4 sample. The release rate of USP-C6 shows catastrophic release as it releases from 3 min (6.08 ppm) to 6 min (36.91 ppm) and then to 9 min (80 ppm) and becomes constant (Table 3). Giroto et al, [67] stated that the urea release rate can be controlled by adding the plasticizer into coating material which can enhance the binding interactions between urea and starch.

The USP-M2 sample shows a diffusional release of urea as it releases gradually from 3 to 9 min (Table 3). However, from 9 to 12 min diffusion increases slightly after which mature stage release has reached. While Table 3 indicates that the release of urea from USP-M4 starts at a very low value (2.75 ppm) following the diffusion release at 6 min (52.75 ppm). The initial release gap is quite large than any other coated urea. It continues to increase like this from 9 to 12 min, after which the release from the coating became constant. In the case of USP-M6, the urea releases gradually with a diffusional release mechanism from 3 to 9 min. Then after 12 min, the urea release rate became constant. It can be concluded here that from all coating combinations with MA, USP-M4 showed the slowest release due to its large initial release gap.

The efficiency of coated and uncoated urea samples was found at 9 min using Eq. (2). The best results were provided by USP-A2 and USP-C2 as observed from Fig. 5.

Uncoated urea sample released after 6 min due to a quick release of all nitrogen content. Sample USP-A2 shows the highest efficiency of 70.10% whereas USP-A4 and USP-A6 show less efficiency of 9.06% and 0%. The efficiency of USP-C2 is 50.74%, which is moderate and is acceptable. With the increase in the concentration of CA, efficiency starts

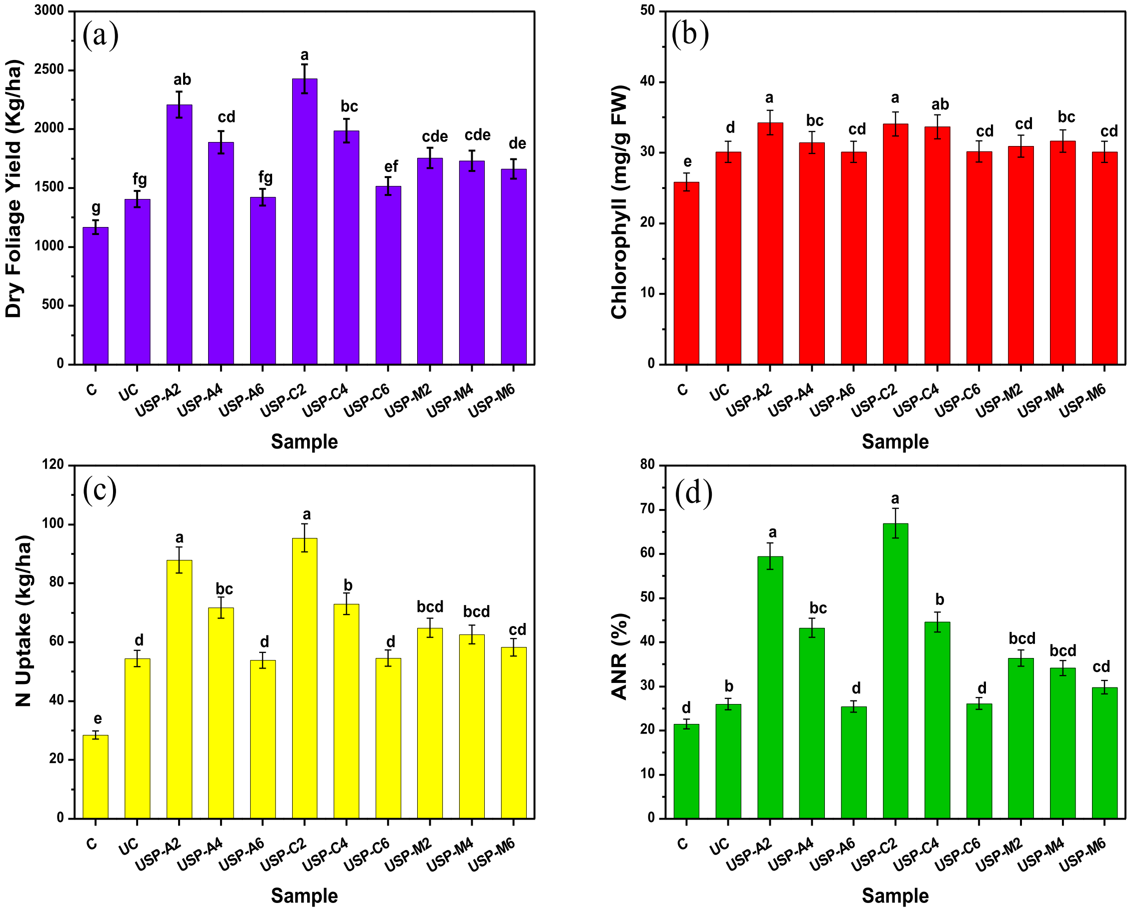

Fig. 6. Effect of uncoated and coated urea samples on; (a) Dry foliage yield (b) Chlorophyll content (c) N-uptake measurements and (d) ANR of spinach plants. Letters on the bars indicate the differences among treatments at 5% level probability. Error bars show standard error of the mean (n=4).

decreasing in USP-C4. It decreased to 14.28% in USP-C4 and reduced to 0% with a further increase of CA in USP-C6.

All combinations of coating material with maleic acid showed very low efficiencies. USP-M2 shows an efficiency of 5.83% which decreases to 3.6% in the case of USP-M4 and then to 1.88% for USP-M6.

Fig. 5 shows that samples USP-A6 and USP-C6 has 0% efficiency values at 9 min due to their quick release before this time but still they retain longer than uncoated urea. Ibrahim et al, [36] observed the release rate of urea coated with mixtures of gypsum and sulphur. They found that the efficiency of urea coated with gypsum-sulphur composition (20 wt%) increased to 26% than uncoated urea which supports the coating of urea for slow release.

Biomass yield and nutrient uptake

The influence of biodegradable coating of urea prills on the foliage yield, chlorophyll content, nitrogen uptake and apparent nitrogen recovery (ANR) is determined and presented in Fig. 6. All coated urea samples provided higher yields than uncoated urea prills and control plants (without fertilizer). In the case of dry foliage yield of spinach plants, USP-C2 showed the highest yield (2428 ± 83 kg/ha) followed by USP-A2 (2208 ± 92 kg/ha) and the lowest yield was obtained from uncoated urea (1168 ± 66 kg/ha) among all urea samples (Fig. 6 (a)). While in the case of chlorophyll content, not appreciable differences were observed among all coated and uncoated samples. The highest chlorophyll content was obtained in case of USP-C2 (34 ± 0.4 mg/gm) and USP-A2 (34 ± 0.6 mg/gm) and USP-A4 samples (34 ± 0.6 mg/gm).

The lowest was in case of uncoated urea (30 ± 0.8 mg/gm), USP-A6 (30 ± 1.7 mg/g), USP-C6 (30 ± 0.5 mg/gm), USP-M6 (30 ± 0.8 mg/gm) which decreased more in case of control plants (26 ± 0.6 mg/gm) (Fig. 6 (b)). The N uptake measurement results were similar to dry foliage matter in trend, in which the highest N-uptake measurement was presented by USP-C2 (95 ± 6 kg/ha) followed by USP-A2 (88 ± 4 kg/ha). While uncoated urea showed the lowest N-uptake (54 ± 6 kg/ha) among all fertilizers and this value decreased further in the case of control plants (28 ±3 kg/ha) as can be seen from Fig. 6 (c). Similarly, USP-C2 (67 ± 6%) showed the highest ANR measurements followed by USP-A2 (59 ± 4%) and the lowest were in the case of uncoated urea prills (26 ± 3%) application (Fig. 6 (d)). It can be concluded that the highest yields, N uptake and ANR of spinach plants are obtained in the case of USP-C2 and USP-A2 use.

This can be related to the delaying of urea hydrolysis from USP-C2 and USP-A2 samples. This delay in hydrolysis synchronized N release from coated urea that matched well with the N requirements of soil [68,69]. The obtained results of urea application effects on spinach plants' growth factors are in strong agreement with the delay in the urea release process by encapsulation as obtained from urea release rates (Table 3). Geng et al, [35] observed the effect of polymer-coated urea (PCU) on the cotton plants and compared its effect with uncoated urea. They observed that PCU increased the yield of lint plants by 5.54–11.17% than uncoated urea. They also found that the nitrogen recovery efficiency of PCU was 31.02% higher than uncoated urea in the case of cotton plants.

Conclusion

In this work, novel encapsulated urea samples were prepared using a fluidized bed coater/granulator. The starch (10%) and PVA (5%)

were used in fixed concentration while AA, CA and MA were used in different concentrations (2 to 6%) for the preparation of coating formulations. The prepared coated urea fertilizers were then subjected to SEM, FTIR, XRD, crushing strength and urea release measurements to check their surface morphology, crystallinity, physical strength and urea release rate. The best combination was selected based on the urea release rate test. Different results verified USP-A2 and USP-C2 to be the best-coated urea samples as they have shown the hardest physical barrier. The urea release rate of these samples was considered best with 70.10 and 50.74% releasing efficiency. This was also verified from crushing strength data that showed 12.08 and 13.67 N values for USP-A2 and USP-C2 respectively. In addition, USP-A2 and USP-C2 showed satisfactory results when applied to spinach plants by providing the highest dry foliage yield (2208 ± 92 and 2428 ± 83 kg/ha), chlorophyll (34 ± 0.6 and 34 ± 0.4 mg/gm), N-uptake (88 ± 4 and 95 ± 6 kg/ha) and ANR (59 ± 4 and 67 ± 6%). For future perspectives, the prepared coated fertilizers should be investigated on plants other than spinach and in different soil conditions to check their agronomic performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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