Release behavior of oxyfluorfen polyurea capsules prepared using PVA and kraft lignin as emulsifying agents and phytotoxicity study on paddy

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ABSTRACT
Polyurea microcapsules containing oxyfluorfen herbicide were synthesized by interfacial polymerization reaction between toluene diisocyanate and ethylene diamine at various core to shell ratios using green solvent \textit{N}-\textit{N}-dimethyldecanamide as carrier medium and using biodegradable PVA203S and Kraft lignin grade (varying molecular weight) as the emulsifying agent. The study was done to understand the effect of stirring rate on preparing microcapsules and find out how the process conditions changed the attributes of microcapsules such as particle size distribution, encapsulation efficiency and release kinetics. The formation of capsules was confirmed by FT-IR, SEM and TGA. The study indicated that the encapsulation efficiency decreased with increasing core to shell ratio. The change in release kinetics was based on the stirring rate and was dependent on the pH of release medium. Particle size distribution was influenced by the agitation speed during formation of emulsion. Kraft lignins of varying molecular weight were used to synthesize the polyurea capsules. It was found that capsules with high molecular weight lignin showed slow and sustained release. Synthesized polyurea capsules was subjected to safety study on paddy crop and compared with commercially available oxyfluorfen and was found to be safe for use on paddy crop.

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1. Introduction
Chemical pesticides are used to control pests, however, their random use has adversely affected the environment by polluting atmosphere and groundwater (1). Microcapsules have become a subject of infinite interest in addressing the environmental concern (2) and have been used for various industrial applications (3). When performance of an active content needs to be protected or degradation of active ingredient has to be controlled, then microencapsulation becomes a good option (2, 4–6). For example, microencapsulation can control the release of the active ingredient from the wall forming material and can also minimize the number of pesticidal application (7).

The microcapsules range in the size of 1–100 micron in which the active material is encapsulated by a natural or substituted polymeric membrane (7). Microencapsulation is a process that allows demarcating the active
material from the surroundings by forming capsules (8). Numerous methods have been recommended for controlling the release of the core material from the shell (9). Process of forming microcapsules in pesticidal application is done by interfacial emulsion polymerization (10, 11). The capsules formed by this method show good thermal properties (5).

There are numerous methods for encapsulation for example, interfacial polymerization (12–14); in situ polymerization (15, 16); complex agglomeration and heterogeneous radical polymerization (17, 18) and solvent evaporation (19, 20).

Nowadays, interfacial polycondensation is widely applied to microencapsulate the core material using various polymeric shells, mostly polyurea (21, 22). The reaction of isocyanates with amines is faster than alcohols and water, therefore, they are mostly used for microencapsulation process by interfacial emulsion polymerization wherein an accelerated reaction is required to prevent the emulsion to destabilize or the wall to deform (5).

Oxyfluorfen (2-Chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene) belongs to diphenyl-ether class of herbicides and is effective in controlling grasses in various crops. Existing product of oxyfluorfen is in emulsifiable concentrate (EC) form and contains harmful solvents such as xylene, cyclohexanone, that causes environmental pollution. Phytotoxicity is observed on rice crop when oxyfluorfen EC is used at a rate of 0.5 kg/ha during the initial growth period, however, the crop recovers with time (23). Phytotoxicity is also observed on rice crop after 6 days of transplantation, when oxyfluorfen is used at low concentration of 0.1 kg/ha (24).

Capsule suspension (CS) synthesized using microencapsulation process helps to minimize phytotoxicity and damage to paddy crop. For plant protection, microcapsule formulations of pesticides have an edge over conventional formulations because they not only effectively eliminate phytotoxicity but also provide several advantages like reduced degradation, decreased dermal toxicity, and reduced environmental pollution (25).

Polyvinyl alcohol has also been used as a watersoluble polymer, which is biodegradable in aerobic and anaerobic conditions (26). Kraft lignins are also considered to be biodegradable (27). Lignin is second most natural material found on the earth in ample quantities. From lignin, lignosulphonate and kraft lignin’s are obtained (28). 85% of the total lignin production is through Kraft pulping process, which is the major method for changing softwood into pulp. The method also provides higher yields compared to other alkaline processes used in the industry. In an alternative process, 90–95% lignins are dissolved in liquor containing sodium hydroxide and sodium sulphite. Pulping process involves conversion of wood into pulp where the lignins are broken down to macromolecules and molecular weight of lignin is reduced.

Molecular weight of lignin is an important parameter which affects the properties of the product to function as a dispersant. The molecular weight of lignin depends on the biological resources used and methods applied for isolating and purifying the product. (29). Kraft and sulphite process produce products having different physico-chemical properties. Not much development has been observed in industry on the use of kraft lignin although high value utilization of the product is reported (30).

Kraft lignin is manufactured in abundance in the pulp industry. At present, kraft lignins are formed by pulping of soft wood and are available commercially in large quantities and henceforth demand is bound to increase with course of time, and it is presumed that it will be beneficial for sustaining and generating value as a bioresource (31). Numerous literature have reported the use of lignin. Stirring rate and pH dependency were studied for preparing avermectin lignin polyurea capsules (32). Oil filled microcapsules of kraft lignin were synthesized by creating an oil in water emulsion and cross linking of lignin at the water/oil interface using high intensity ultrasound. The ability of lignin microcapsules to incorporate and release Coumarin-6 was studied (33). Organometallic catalysts, biomimetic catalysis and plasma oxidation were developed for the activation of the environmentally friendly oxidants oxygen and hydrogen peroxide in the oxidative functionalization of lignin and lignin model compounds (34). Lignins have also been used as carriers suitable for loading and release of pesticides, pharmaceuticals, and biological macromolecules (35). Lignin microcapsules containing thymol, 4-bromothymol, 2,4 dibromothymol, and the corresponding O-methylated derivatives were prepared using a sustainable ultrasonication procedure with 50% encapsulation efficiency and slow release of the active ingredient (36). Hollow polymeric, submicrometer-scaled up capsules for use of water remediation were prepared using kraft and alkali lignin as renewable and easily degradable particulate templates (37). Lignin-based pH-responsive nanocapsules were synthesized by grafting lignin with allyl groups through etherification and further dispersed in an oil-in-water miniemulsion system via ultrasonication. The study indicated that release varied in various pH system (38). Microcapsules were also prepared by absorbing chitosan onto colloidal lignin particles and studied for olive oil stabilizion; rapid release of drug was observed in aqueous media (39). Biomaterial lignins were used to prepare hollow nanocapsules in interfacial polyaddition in inverse
miniemulsions. Synthesized cross linked lignin nanocontainers would be loaded with hydrophilic substances, wherein the release is possible by an enzymatic trigger from natural plant extracts enhancing them as potential nanocontainers for agricultural applications (40). Lignin nanocapsules were prepared and loaded with gibberellic acid, the synthetized polymeric nanocapsules were used as biocompatible vectors for delivery of bioactive compounds to plants (41). Lignin isolated using the acidic dioxane method from subabul stems was used to entrap the herbicide Diuron by nanoprecipitation. Release of Diuron from the LNPs immersed in aqueous buffer solutions increased with increasing pH value from 5 to 9 and was significantly slower compared to the dissolution of bulk Diuron or commercial Diuron formulation (42). Lignin microcapsules were prepared from organosolv and ionic solution for encapsulation and controlled release of herbicide atrazine, study indicated that higher encapsulation efficiency is obtained with organosolv lignin particles compared to ionic lignin systems and dispersed phase effected the morphology of capsules (43). Kraft lignins were modified through esterification of its hydroxyl groups with methacrylic anhydride and then lignin carriers with different morphologies were produced by a combination of mini emulsion polymerization and a solvent evaporation process, which will have useful application as novel drug delivery vehicle in agriculture (44). Engineering of hybrid nanocapsules from lignin/fatty acids and size controlled colloidal synthesis by aqueous precipitation is reported in the literature having application as phase change materials (45). Lignin nanoparticles offer many opportunities for value-added applications of lignin. (46). Dipotassium phosphate and urea were coated by lignin and formaldehyde to prepare microcapsules of NPK. Fast release of the nutrients was observed at lower pH (47). Lignin polyureamic microcapsules (LPMC) were synthesized by interfacial polymerization based on Pickering emulsion templates of lignin particle-stabilized oil in water to encapsulate avermectin (48). Pickering emulsion is stabilized by lignin nanoparticles to microencapsulate the active 1-Tetradecanol via polymerization of acrylates for thermal management purpose. High encapsulation would be achieved when the core/shell mass ratio was 2:1, and 10 wt% of the crosslinking monomer pentaerythritol tetraacrylate (PETRA) was used (49). Recent studies have shown that kraft lignin can also function as dispersants, bioplastics, and fuel for transportation (50).

Not much research work has been done on the benefits/application of kraft lignin dispersants having varying molecular weight as emulsifying agent for microencapsulation process and its effect on release kinetics and safety to crop.

In the first set of present study, polyurea microcapsules containing herbicide oxyfluorfen were prepared by reacting toluene diisocyanate (TDI) with crosslinking amine (EDA) using biodegradable polyvinyl alcohol as water soluble emulsifying agent and green solvent N,N-dimethyldecanamide as a carrier medium in the encapsulation process. This study focused on establishing process conditions to prepare polyurea microcapsules by interfacial polymerization. The work also reports the outcome of process condition affecting the properties of the microcapsules such as morphology, particle size distribution, encapsulation efficiency and release kinetics of the microcapsules under varying pH conditions. The outcome of core to shell ratio and stirring rate, on particle size and encapsulation efficiency was also studied to optimize the process of preparing oxyfluorfen microcapsules. The effect of biodegradable kraft lignin dispersants having different molecular weight as emulsifying agent on the release kinetics and encapsulation efficiency of the microcapsules was also studied. We believe that the work would provide basic references for industrial production of oxyfluorfen microcapsules suspension. The structure of oxyfluorfen and N,N-dimethyldecanamide (solvent) is represented in Figure S1.

2. Materials and methods
2.1. Raw materials
Toluene diisocyanate (TDI) and ethylenediamine (EDA) were purchased from SD fine chemicals and Huntsman, respectively. Oxyfluorfen technical was purchased from Willowood chemicals. PVA203S grade (hydrolysis value of 88) was purchased from Sekisui. N,N dimethyldecanamide and kraft lignin grade surfactants (varying molecular weight) were obtained from Solvay and Ingevity (USA), respectively.

2.2. Preparation of oxyfluorfen microcapsules
The flow chart and general scheme for the preparation of microcapsules by interfacial polymerization is shown in Figure 1. The formation of microcapsules was optimized by various experimental parameters as depicted in Tables 1 and 2 which shows various types of kraft lignin used for the study. TDI was used as the first monomer while cross linking amine (ethylene diamine) was subsequently used as second monomer.

Core to shell ratio (6:1) was calculated as follows: 17 g of oxyfluorfen technical considered in experiment number...
E1 is the core material and shell forming material is TDI and EDA. Shell forming material on dry basis is 2.80 g, therefore for 17 g of oxyfluorfen core material, shell material used is 3.4 g which corresponds to 5:1 ratio. Similarly calculated for core to shell ratio 4:1.

2.3. Formation of the microcapsules

Experiment no E1: 10 g of N-N-dimethyldecanamide was taken in a 50-ml three necked round bottom flask and heated to 50 °C in a water bath with constant stirring. 17 g of oxyfluorfen technical (98% purity) was slowly poured into it with constant stirring. Heating was continued till oxyfluorfen dissolves in the solvent and temperature raised to 60 °C. Further, 2.42 g of TDI was added and dissolved to form the organic phase.

67.13 g of water was taken in a 250-ml beaker and heated to 60 °C. 2 g of poly vinyl alcohol powder (hydrolysis value 88) was slowly dissolved in it under stirring speed of 100 rpm. The organic phase was added to the aqueous phase at 60°C. Emulsification was carried out for 15 min using rotor/stator homogenizer from IKA. The revolution speed of emulsification was kept at 5000 rpm. Oil-in-water emulsion formed was then transferred to a 200-ml round bottom flask kept in water bath.

1.45 g of cross-linking amine solution of 60% concentration was slowly added to the reaction mixture under stirring at 350 rpm and the reaction was maintained for 3 h at 60 °C to obtain microcapsules in slurry form.

Reaction was initially monitored by checking the formation of capsules using optical microscope. All the experiments reported here were prepared by the above methodology, wherein the quantity of oxyfluorfen technical, N-N-Dimethyldecanamide and PVA was kept constant.

Experiment no E2-E9: The quantity of hydrophobic monomer (TDI), cross-linking amine (ethylenediamine) and stirring rate was changed to understand the outcome of core/shell ratio on encapsulation efficiency, particle size distribution and release kinetics. Further studies were done by replacing 2 g of polyvinyl alcohol (PVA) with 2 g of kraft lignin sulphonate of low molecular weight at varying core to shell ratio and stirring rate as shown in Table 3a. Encapsulation efficiency of this experiments was studied and based on the encapsulation efficiency, core to shell ratio of 5:1 at stirring rate of 7500 rpm was selected for further studies.

Kraft lignin sulphonates having varying molecular weight as explained in Table 2 were used as emulsifying agent for preparing polyurea capsules using core to shell ratio of 5 : 1 at stirring rate of 7500 rpm (Experiment no K2 to K7). Kraft lignin having different molecular weight...
Table 3a. Experimental and operating conditions using kraft lignin low molecular weight (Polyfon O) as emulsifying agent.

| Exp | TDI (g) | EDA Solution 60% (g) | Water (g) | Core to Shell ratio | Stirring rate (rpm) |
|-----|---------|----------------------|-----------|---------------------|---------------------|
| A   | 2.42    | 1.45                 | 67.13     | 6 : 1               | 5000                |
| B   | 2.42    | 1.45                 | 67.13     | 6 : 1               | 7500                |
| C   | 2.42    | 1.45                 | 67.13     | 6 : 1               | 10,000              |
| D   | 2.93    | 1.76                 | 66.31     | 5 : 1               | 5000                |
| E   | 2.93    | 1.76                 | 66.31     | 5 : 1               | 7500                |
| F   | 2.93    | 1.76                 | 66.31     | 5 : 1               | 10,000              |
| G   | 3.5     | 2.1                  | 65.4      | 4 : 1               | 5000                |
| H   | 3.5     | 2.1                  | 65.4      | 4 : 1               | 7500                |
| I   | 3.5     | 2.1                  | 65.4      | 4 : 1               | 10,000              |

Table 3b. Experimental and operating conditions using kraft lignin having different Molecular weight as emulsifying agent.

| Exp no | TDI (g) | EDA Solution 60% (g) | Water (g) | Core to Shell ratio |
|--------|---------|----------------------|-----------|---------------------|
| K2 (M_w 2900) | 2.93 | 1.76 | 66.31 | 5 : 1 |
| K3 (M_w 4300) | 2.93 | 1.76 | 66.31 | 5 : 1 |
| K4 (M_w 9000) | 2.93 | 1.76 | 66.31 | 5 : 1 |
| K5 (M_w 10200) | 2.93 | 1.76 | 66.31 | 5 : 1 |
| K6 (M_w 11000) | 2.93 | 1.76 | 66.31 | 5 : 1 |
| K7-B (M_w 13400) | 2.42 | 1.45 | 67.13 | 6 : 1 |
| K7-E (M_w 13400) | 2.93 | 1.76 | 66.31 | 5 : 1 |
| K7-H (M_w 13400) | 3.50 | 2.1 | 65.40 | 4 : 1 |

3. Characterization of microcapsules

3.1. Fourier transform infrared spectroscopy

The microcapsules suspension was centrifuged, and yellow capsule powder was obtained which was washed initially with 30% aqueous solution of ethanol, and finally thrice with deionized water. The microcapsules were dried at ambient temperature for 24 h and used for analysis. FT-IR was recorded on a FT-IR Bruker model Alpha-2 and recording of spectra was done in the range of 4000 and 500 cm⁻¹ at 4 cm⁻¹ resolution. The functional groups of polyurea microcapsules were examined.

3.2. Measurement of encapsulation efficiency

The encapsulation efficiency of microcapsules was analyzed by weighing a known amount of the reaction mixture with water and mixing at ambient temperature. To this mixture, 50 ml n-hexane was added for extracting the active content. The amount of the active content in the hexane layer was determined by gas chromatography using DB-1 column. The obtained oxyfluorfen content is represented as EEA (Easily extracted active content) and encapsulation efficiency is calculated as 100-%EEA (51).

3.3. Particle size analysis

The particle size distribution of polyurea microcapsules was analyzed by utilizing a laser particle size analyzer, Malvern size model Mastersizer 2000. All the analysis of the samples were done at ambient temperature.

3.4. Morphology analysis by SEM

Polyurea microcapsules were characterized by scanning electron microscope (JEOL JSM IT-200).

3.5. Thermogravimetric analysis

The thermal stability of microcapsules was analyzed by using TGA analyzer (TA instrument SDT Q600). 7 mg sample was heated in the range of 24–450 °C at a rate of 10 °C/min in a flow of 60 ml/min of nitrogen used as purging and protective gas.

3.6. Release profile of the microcapsules

The release profile of oxyfluorfen from the microcapsules was evaluated from the calibration graph as shown in Figure S2. Known concentrations of oxyfluorfen solutions were prepared in hexane and absorbance (λ_max) were measured in the range 200–600 nm by using UV–Visible spectrophotometer. In this study, a prominent peak at 205 nm was observed. From the calibration curve, unknown concentration of oxyfluorfen was determined. The slope and intercept values were calculated to be 0.020 and 0.0129, respectively, with R² = 0.9985, using the equation y = mx + c.
1 g of microcapsules (reaction product) was weighed in a 250-ml conical flask containing 200 ml of water and the solution was agitated at 150 rpm in an incubator shaker. An aliquot sample of known volume (10 ml) were withdrawn at specific time intervals and added in 50 ml of hexane to extract oxyfluorfen active and the absorbance of hexane layer solution was analyzed by UV–Visible Spectrophotometer at 265 nm. From the absorbance values, concentration of oxyfluorfen was calculated from slope and intercept. Each aliquot withdrawn was replaced by 10 ml of dilution medium to maintain a constant volume in the flask.

3.7. Phytotoxicity assessment

The prepared polyurea capsules and marketed sample of oxyfluorfen 23.5% EC were applied on paddy crop to evaluate the phytotoxicity. The suitability of microencapsulated product on the paddy crop as control medium was evaluated by phytotoxicity assay. The visible phytotoxicity marks were assessed on the 10th day of application and the visible marks were assessed based on necrosis and tip burning.

All the phytotoxicity trials were conducted in single plot. 25 days nursery seedlings were transplanted in the main field, after third day of the transplantation, both the encapsulated product and commercially available market sample of oxyfluorfen 23.5% emulsifiable concentrate were applied by manually handled sprayer fitted with flat fan nozzle.

Three sample of oxyfluorfen microcapsules, prepared using core to shell ratio of 5 : 1 and stirring rate of 7500 rpm is considered for phytotoxicity study. Experiment no. 5 (prepared using PVA as emulsifying agent), K1 (capsules prepared using low molecular kraft lignin) and K7 (capsules prepared using high molecular kraft lignin) were applied in the field at three different doses along with three doses of market sample of Oxyfluorfen 23.5% EC at dose rate of 650–1000 ml/ha.

4. Results and discussion

4.1. Functional group analysis

Figure 2(a) shows the FTIR spectra of polyurea capsules formed using TDI and EDA: core material is oxyfluorfen Technical, blank polyurea microcapsules and oxyfluorfen polyurea capsules. Toluene-2,4-diisocyanate reacts with ethylene diamine to form urea linkage. As shown in Figure 2(a), strong N-H stretching vibration is observed at 3300 cm⁻¹ in the product and polyurea blank capsules while the vibrations were not seen in the spectra of core material, indicating that the reaction as taken place between TDI and amine. The C–H stretching vibrations were seen at 2926 and 2856 cm⁻¹. NCO peak was not observed at 2270 cm⁻¹ indicating that the reaction has occurred between hydrophobic monomer and the cross-linking amine, and presence of N–H and C=O absorption bands further confirm the reaction is completed between TDI and EDA.

Core material showed stretching vibrations of N–O at 1576 cm⁻¹ as shown in Figure 2(b). Absence of this peak in the polyurea blank capsules and appearance in the synthesized product further indicate that the polyurea capsules are formed containing the core material. Polyurea capsules also exhibited strong carbonyl stretching at 1650 cm⁻¹.

4.2. Encapsulation efficiency

Table 4 represents the encapsulation efficiency of polyurea capsules formed using ethylenediamine as monomer, PVA as emulsifying agent under various
conditions of stirring rate and core to shell ratio. The core to shell ratio experimented for the studies were 6:1, 5:1, and 4:1. As the core to shell ratio was increased, the encapsulation efficiency decreased. This may be possible since with the reduction in quantity of wall forming material, the resultant polyurea wall membrane would not completely cover the core material. An increase in stirring rate from 5000 to 10,000 rpm did not have much effect on the encapsulation efficiency. In this study, the effectiveness of the encapsulation process was established to be in the range of 95.47–98.7%. The study was done in triplicates.

Table 5 represents the encapsulation efficiency of polyurea capsules formed using ethylenediamine as monomer, kraft lignin as emulsifying agent under various conditions of stirring rate and core to shell ratio of 6:1, 5:1, and 4:1. As the core to shell ratio was increased, the encapsulation efficiency decreased, which is very similar to the study using PVA as emulsifying agent as displayed in Figure 3 for PVA based polyurea capsules and Figure 4 for kraft lignin based polyurea capsules. An increase in stirring rate from 5000 to 10,000 rpm did not have much effect on the encapsulation efficiency. In this study, the effectiveness of the encapsulation process was established to be in the range of 94.05–96.77%. The study was done in triplicates.

Table 5. Encapsulation efficiency of polyurea capsules at different stirring rate and varying core to shell ratio for capsule prepared using lignin as emulsifying agent (Experiment no K1, A to I).

| RPM | Core to shell ratio | Easily extractable active content (EEA) | SD (±) | Encapsulation efficiency (%) |
|-----|---------------------|----------------------------------------|--------|-----------------------------|
| 5000 m | 6:1                 | 5.73                                   | 0.082  | 94.27                       |
| 7500 n | 5:1                 | 5.95                                   | 0.094  | 94.05                       |
| 10,000 o | 4:1                | 5.50                                   | 0.108  | 94.50                       |
| 5000 m | 6:1                 | 4.57                                   | 0.068  | 95.43                       |
| 7500 n | 5:1                 | 4.85                                   | 0.071  | 95.15                       |
| 10,000 o | 4:1                | 4.73                                   | 0.085  | 95.27                       |
| 5000 m | 6:1                 | 3.70                                   | 0.141  | 96.30                       |
| 7500 n | 5:1                 | 3.23                                   | 0.094  | 96.77                       |
| 10,000 o | 4:1                | 3.50                                   | 0.163  | 96.50                       |

mCore to shell ratio 6:1.

nCore to shell ratio 5:1.

oCore to shell ratio 4:1.

Standard deviation n = 3.

Table 4. Encapsulation efficiency of polyurea capsules at different stirring rate and varying core to shell ratio using PVA as emulsifying agent.

| RPM | Core to shell ratio | Easily extractable active content (EEA) | SD (±) | Encapsulation efficiency (%) |
|-----|---------------------|----------------------------------------|--------|-----------------------------|
| 5000 m | 6:1                 | 4.21                                   | 0.042  | 95.79                       |
| 7500 n | 5:1                 | 4.53                                   | 0.103  | 95.47                       |
| 10,000 o | 4:1                | 3.12                                   | 0.111  | 96.88                       |
| 5000 m | 6:1                 | 2.10                                   | 0.066  | 97.90                       |
| 7500 n | 5:1                 | 2.22                                   | 0.085  | 97.78                       |
| 10,000 o | 4:1                | 2.50                                   | 0.082  | 97.5                        |
| 5000 m | 6:1                 | 1.55                                   | 0.111  | 98.45                       |
| 7500 n | 5:1                 | 1.30                                   | 0.082  | 98.70                       |
| 10,000 o | 4:1                | 1.59                                   | 0.084  | 98.41                       |

mCore to shell ratio 6:1.

nCore to shell ratio 5:1.

oCore to shell ratio 4:1.

Standard deviation n = 3.

Figure 3. Encapsulation efficiency of PU microcapsules at varying core to shell ratio using PVA as emulsifying agent, at stirring rate of 7500 rpm.

Figure 4. Encapsulation efficiency of PU microcapsules at varying core to shell ratio using Lignin as emulsifying agent, at stirring rate of 7500 rpm.
4.3. Particle size measurement

Microcapsule size is an important parameter that affects the release rate of the core material. In this study, particle size and distribution were analyzed by Malvern laser particle size analyzer. Figures 6–8 display particle size distribution obtained using varying stirring rate and core/shell ratio. Experiment nos. 3, 6 and 9 show that when agitation speed is increased to 10,000 rpm, the particle size decreased (52), and when the agitation speed is decreased to 5000 rpm (Experiment nos. 1, 4 and 7), the particle size increased, and the particle size distribution becomes non-uniform. This phenomenon is observed in the core to shell ratio of 6:1, 5:1 and 4:1. From the results, no remarkable effect was observed due to the core to shell ratio. With increase in stirring rate, size distribution becomes narrower. Particle size is diminished with the agitation speed (53). Microcapsules having particles of similar size are formed at 7500 and 10,000 rpm, whereas microcapsules having particles of varying size are formed at 5000 rpm.

During the process of formation of microcapsules, agitation speed, viscosity and surface tension of the reaction mass determines the droplet size. Agitation speed helps the droplets to disperse, while viscosity and surface tension of the reaction mass prevents the droplets to disperse. As the agitation speed is increased during the emulsification process, agitation force gets stronger than viscosity and surface tension forces and therefore, the droplets are continuously broken down to smaller particles (1). Droplet size decreases with increasing stirring rate as stirring rate is proportionate to the rate of stirring (53).

Experiment nos. 1, 2, and 3 having core shell ratio of 6:1, the mean particle size is decreased from 20.32 to 7.32 μm as the stirring rate is increased from 5000 to 10,000 rpm as shown in Figure 5. Experiment nos. 4, 5, and 6 having core shell ratio of 5:1, the mean particle size is decreased from 17.57 to 7.4 μm as the stirring rate is increased from 5000 to 10,000 rpm as shown in Figure 6. Experiment nos. 7, 8, and 9 having core shell ratio of 4:1, the mean particle size decreased from 20.17 to 7.1 μm as the stirring rate is increased from 5000 to 10,000 rpm as shown in Figure 7. The results indicate that the particle size is decreasing with increasing stirring rate.

4.4. Study of surface morphology

SEM images of oxyfluorfen polyurea microcapsules are presented in Figure 8. Studying the morphology has considerable importance in understanding the microencapsulation process (54), pp 23–36. Figure 8(a–c) shows polyurea microcapsules with EDA/diisocyanate using PVA as the emulsifying agent at various stirring rates. As seen from the figure when the stirring rate increases, particle size reduces. The microcapsules are spherical, with a smooth surface. Crystal formation is seen in some SEM images indicating that all the core material...

### Table 6. Encapsulation efficiency of polyurea capsules at 7500 rpm using different grades of kraft lignin dispersants at core to shell ratio of 5:1.

| Batch no | Easily extractable active content (EEA) | SD (±) | Encapsulation efficiency (%) |
|----------|----------------------------------------|--------|-----------------------------|
| K1       | 4.85                                   | 0.071  | 95.15                       |
| K2       | 3.56                                   | 0.146  | 96.44                       |
| K3       | 3.82                                   | 0.085  | 96.18                       |
| K4       | 2.94                                   | 0.057  | 97.06                       |
| K5       | 2.65                                   | 0.041  | 97.35                       |
| K6       | 3.12                                   | 0.103  | 96.88                       |
| K7       | 3.32                                   | 0.155  | 96.68                       |

Standard deviation n = 3.
is not encapsulated. Analysis by the GLC method indicated that unencapsulated oxyfluorfen content to be in the range of 3–4.5%. Figure 9(d) shows polyurea microcapsules with EDA/diisocyanate using kraft lignin as the emulsifying agent (Experiment K7). Microcapsules were somewhat spherical, wrinkled and had obvious depressions. Appearance of shrinkages may be attributed to the solvent and core material being released resulting in volume been created internally. In other words, the solvent and the core material provided internal free volume which led to shrinkage of wall material. Figure S3 shows capsules prepared using Kraft lignin of varying molecular weight as emulsifying agent, in all the SEM images it is seen that microcapsules are spherical and somewhat wrinkled. Literature data suggests that the Interaction of inhomogeneous reaction kinetics, liquid induced shear forces and wall forming forces, may result in wrinkling of the capsules (55). The surface morphology helps in understanding that EDA polyurea capsules prepared using PVA as emulsifying agent has different oxyfluorfen release kinetics compared to EDA polyurea capsules prepared using kraft lignin as emulsifying agent.

4.5. Thermo gravimetric analysis

Figure 9 displays the TGA diagrams of core material and polyurea microcapsules synthesized from ethylenediamine. Loss in weight of the sample verifies that the reaction has taken place between TDI and ethylenediamine and polyurea capsules are formed. (56, 57). As shown in Figure 9, initial weight loss can be factored due to water loss, second weight loss of 31.94% in the range of 216–255 °C is due to evaporation and degradation of the active material oxyfluorfen. Third weight loss of about 28.70% in the range of 255–450 °C is due to the degradation of polyurea wall material. Also, the weight loss of oxyfluorfen initiates at 180 °C and gets completed at 280 °C correlating to the evaporation of oxyfluorfen.

4.6. Release kinetics of oxyfluorfen in water

Release study of oxyfluorfen from the microcapsules was evaluated at different time intervals for period of 168 h. The release studies were done in triplicates. From Figures 10–12, and Table S1 it is observed that core to shell ratio had huge impact on the release behavior of oxyfluorfen capsules. As the core to shell ratio is decreased, the release rate decreases which can be
attributed to increased wall thickness of the capsules formed due to higher loading of shell forming material. It is observed that as the stirring rate of the emulsion is increased from 5000 to 10,000 rpm, the release of the active content from the core was faster (85% to 97% Experiment no 1–3), (68% to 82% Experiment no 4–6) and (59% to 78% Experiment no 7–9) which can be attributed to the thin wall formation or smaller particle size at high stirring rate. From the release study, it is concluded that core to shell ratio and stirring rate impacts the release behavior of the capsules from the shell.

Figure 13 and Table S2 show the effects of release kinetics on the polyurea capsules formed using 5 : 1 core to shell ratio and at stirring rate of 7500 rpm using kraft lignin dispersants as emulsifying agents. It is observed that as the kraft lignin molecular weight is increased, release rate decreases. As seen in (Experiment K7, molecular weight 13,400 MW) release of the core material from the shell is slow which corresponds to 48.16%, whereas in Experiment K1 (molecular weight 2400 MW) release is fast and corresponds to 80.36%. (58) have observed that kraft lignin having increased molecular weight has effective dispersion properties due to larger steric forces, thus increasing the effectiveness of the product as dispersant. This research work indicates that the release behavior of the polyurea capsules can be altered depending upon the type of biodegradable kraft lignin dispersant used in the reaction, so microcapsules of desired release can be synthesized in lab.

Extreme water pH can reduce the solubility of some herbicides by preventing some of the product from dissolving and leaving some product suspended in the solution. Insolubilized or suspended herbicide precipitates can block the nozzles during application and thereby
decreasing the delivery of the active ingredient to the target site. Therefore, two extreme pH conditions (pH 4 and pH 10) were selected for the study to understand the effect of pH on the release behavior of herbicide release from the capsules during application (59). This study will help in designing the composition of the final formulation during manufacturing of the product at commercial scale.

The release behavior of oxyfluorfen microcapsules of Experiment nos. E2, E5, E8 (Stirring rate 7500 rpm) were studied at different pH conditions. pH of the medium used for the study was 4 and 10 which was prepared by hydrochloride and sodium hydroxide, respectively. Temperature of the medium was kept at 25 °C and medium was agitated at 150 rpm in incubator shaker. The release behavior of oxyfluorfen microcapsules prepared using lignin as emulsifiers was also studied to understand the effect of pH. Experiment no. K1, oxyfluorfen capsules prepared using low molecular weight lignin and Experiment no K7, oxyfluorfen capsules prepared using high molecular weight lignin (Stirring rate 7500 rpm and core to shell ratio 6:1, 5:1 and 4:1) were selected for the study.

Figures 14 and 15 show the outcome of varying pH values (4,10) on the oxyfluorfen release behavior prepared using PVA as emulsifying agent. Fast release is observed at pH 4. Initial release rate was found to be 5%, 15% and 25% for core shell ratio of 4:1, 5:1 and 6:1 respectively indicating a burst mechanism. Initial release rate was constant at pH 10 for the entire core to shell ratio studied.

Figures 16 and 17 show the outcome of varying pH values (4,10) on the oxyfluorfen release behavior prepared using low molecular weight Lignin as emulsifying agent (Experiment no K1). Fast release is observed at pH 4. In this case, initial release rate was found to be 10.2%, 17.2% and 21.1% for core shell ratio of 4:1, 5:1 and 6:1 respectively indicating a burst mechanism. In case of pH 10, the initial release was constant for all the core to shell ratio studied.

Figures 18 and 19 show the outcome of varying pH values (4,10) on the oxyfluorfen release behavior prepared using high molecular weight lignin as emulsifying agent (Experiment no K7). In this case, initial release is constant at pH 4 and 10. Sustained release is seen in both the pH values indicating that the molecular weight used is also important contributing factor for the release of the core material along with pH value.
Different release behavior is due to the difference in solubility of kraft lignin in different pH conditions. Kraft lignins have better solubility at higher pH value, at pH 4 the solubility is 60% and at pH > = 7 the solubility is 100% (60).

Change in release kinetics is observed based on the pH of the medium used for the study. The release kinetics was analyzed by using the Korsmeyer–Peppas model, $M_t/M_\infty = k^n t^n$, $t$ stands for time, $k$ and $n$ are constant and are calculated as shown in Table 8 using DD solver (61). Release mechanism of the core material from the shell can be predicted by $n$ value. It helps to identify various release mechanisms (52, pp 23–36; 62, pp 37–42). The criteria of using $n$ value is based on differentiated mixing mechanism which is affected by various factors and geometries of the pesticide delivery system. Release profile was studied by considering the time taken for release of 50% of oxyfluorfen from the shell. As per Table 7, the release mechanism of the core can be considered as follows: (1) Fickian diffusion or diffusion mechanism wherein characteristic solvent diffusion time is greater than the polymer relaxation time, (2) case II involves the breaking of the polymer matrix by erosion, (3) third mechanism is in between the Fickian case and case II mechanism (63). Accordingly, to adjusted $R^2$ values, the Peppas-model provides a good correlation with the data and is useful in analyzing the release mechanism of the microcapsules (64). In Table 8, value of $n$ is below 0.89 at a pH of 4 which indicates combined mechanism of diffusion and erosion and $n$ value is greater than 0.89 at a pH of 10 indicating erosion mechanism release.

In Table 9, the value of $n$ is below 0.89 at a pH of 4 and 10 for oxyfluorfen capsules prepared using low molecular weight lignin indicating combined

Table 7. Release kinetics value for various delivery system.

| Thin film | Exponent, $n$ | Cylinder | Sphere | Release mechanism |
|-----------|--------------|----------|--------|-------------------|
| 0.5       | 0.45         | 0.43     | Fickian diffusion |
| 0.5 < $n$ < 1.0 | 0.45 < $n$ < 0.89 | 0.43 < $n$ < 0.85 | Anomalous transport (Diffusion mechanism) |
| 1         | 0.89         | 0.85     | Case II transport (Combined diffusion and Erosion mechanism) |
mechanism of diffusion and erosion. The value of $n$ is greater than 0.89 at a pH of 4 for oxyfluorfen capsules prepared using high molecular weight lignin indicating erosion mechanism release and value of $n$ is below 0.89 at a pH of 10 indicating release through combined mechanism of diffusion and erosion. Study indicates that pH of the water is very critical for the release of the core material from the shell and depending upon the pH of water available in the agricultural field, the release of the core from the capsules may vary. Research work also indicates that release is dependent on the type of emulsifying agent used PVA or lignin in preparing the oxyfluorfen capsules and further depends on the molecular weight of lignin.

### 4.7. Phytotoxicity assessment

The phytotoxicity assessment was made based on rating scale as presented in Table S3 (65). When polyurea microcapsules (CS) sample of Oxyfluorfen were applied in the field along with market standard sample of Oxyfluorfen 23.5% EC, initial yellowing and tip burning were observed after second day of application, but in all the treatments of microencapsulated product, fast recovery was observed when compared with market standard as seen in Figure 20(a). The marketed standard sample of Oxyfluorfen EC completely damaged the paddy crop after third day at dose level of 650, 750 ml/ha and at 1000 ml/ha as presented in Tables S4 and S5. Recovery is faster in K7 treated plot compared to K1 treated plot indicating that slow release of the core from the shell is helping in controlling phytotoxicity symptoms.

30th day observation in the field indicated that the crop treated with microencapsulated product exhibited improved growth while crop treated with market sample of oxyfluorfen 23.5% EC was completely damaged and dried as seen in Figure 20(b).

Commercially available sample of oxyfluorfen 23.5% EC completely damaged the crop at 1000 ml/ha dose rate, while the encapsulated polyurea capsules at 1000 ml/ha dose rate, synthesized using PVA and Kraft lignin as emulsifying agents did not damage the crop, as seen in Figure 20(a) after 10 days of application and Figure 20(b) after 30 days of application. This can be explained as follows, when oxyfluorfen 23.5% EC is applied it is immediately incorporated into the medium resulting in phytotoxicity symptoms (66).

![Figure 20a](image-url) (a) Phytotoxicity assessment after 10 days of treatment (1000 ml/ha dose rate). (b) Phytotoxicity assessment after 30 days of treatment (1000 ml/ha dose rate).

![Figure 20b](image-url)
while in case of synthesized polyurea capsules, the release of the active is sustained due to polymeric wall, therefore phytotoxicity symptoms are not seen and no damage to paddy crop can be observed.

5. Conclusion

Our study indicated that the stirring rate and core to shell ratio had impact on release behavior of the microcapsules formed. With increasing stirring rate, fast release of the core from the shell was seen. As the core to shell ratio was decreased the release was slow. The study indicated that the release behavior was pH dependent and also affected by the emulsifying agents used in preparing polyurea capsules. Fast release was observed at pH 4 compared to pH 10 for polyurea capsules prepared using PVA and lignin of low molecular weight as emulsifying agent. Stirring rate also impacted on size distribution, size distribution became narrower, as the stirring rate was altered from 5000 to 10,000 rpm.

Release kinetics behavior was also dependent on the type of kraft lignin used as emulsifying agent in the reaction. Release of the core from the shell was decreased with increasing molecular weight of kraft lignin.

The encapsulation efficiency obtained was in the range of 95.47–98.7% for polyurea microcapsules prepared using PVA as emulsifying agent. The encapsulation efficiency decreased as the core to shell ratio was increased, for polyurea capsules prepared using PVA and kraft lignin as emulsifying agents. The SEM study indicated that the surface of the polyurea capsules was different when using PVA and kraft lignin as emulsifying agents. The microcapsules also reduced the risk of phytotoxicity to paddy crop in comparison to market sample of Oxyfluorfen 23.5%EC. Present research may be very highly useful for industrial preparation of Oxyfluorfen CS having the required release properties based on the type of biodegradable material (PVA or Kraft lignin) used as emulsifying agent for preparation of microcapsules.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

Supporting Information: SI contains Fig. S1 (chemical structure of various components), S2 (calibration curve), S3 (SEM images of capsules prepared using kraft lignin of varying molecular weight) and Table S1 (Release kinetics at different stirring rate and core to shell ratio), S2 (Release kinetics study of polyurea capsules prepared using Kraft lignin dispersants), S3 (Phytotoxicity assessment-rating), S4 (Phytotoxicity assessment-necrosis), and S5 (Phytotoxicity assessment-tip burning).

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