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Machine Learning Model for Nutrient Release from Biopolymers Coated Controlled-Release Fertilizer

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Abstract: Recent developments in the controlled-release fertilizer (CRF) have led to the new modern agriculture industry, also known as precision farming. Biopolymers as encapsulating agents for the production of controlled-release fertilizers have helped to overcome many challenging problems such as nutrients' leaching, soil degradation, soil debris, and hefty production cost. Mechanistic modeling of biopolymers coated CRF makes it challenging due to the complicated phenomenon of biodegradation. In this study, a machine learning model is developed utilizing Gaussian process regression to predict the nutrient release time from biopolymer coated CRF with the input parameters consisting of diffusion coefficient, coefficient of variance of coating thickness, coating mass thickness, coefficient of variance of size distribution and surface hardness from biopolymer coated controlled-release fertilizer. The developed model has shown greater prediction capabilities measured with R^2 equalling 1 and a Root Mean Square Error (RMSE) equalling 0.003. The developed model can be utilized to study the nutrient release profile of different biopolymers'-coated controlled-release fertilizers.

Keywords: controlled-release fertilizer; biopolymer coating; enzymatic degradation; machine learning; gaussian process regression; modelling and simulation

1. Introduction

In the last two decades, the population has risen exponentially, and it is expected to reach 9.7 Billion in 2050 [1]. It is hence increasing the demand for food supply. To grow such a massive quantity of food, the agricultural land required is huge. However, due to industrialization, soil degradation, and climate change, the agricultural land has been reduced in the last two decades [2]. To overcome this problem, researchers developed high efficiency controlled-release fertilizers (CRF). Initially, CRF is coated with non-biodegradable polymers. In the release process

from the synthetic polymer coating, up to 30% [3,4] nutrient used to remain in the shell after the release, and inorganic polymer used to remain in the agriculture field as debris. The solution to the problem was to use biodegradable polymers as the coating materials in CRF. For the coating of CRF's a wide variety of biodegradable polymers have shown positive results in terms of delayed release time, and water-retention property. Zahid et.al [4] have presented a comprehensive review of the biodegradable polymers used in CRF. The biodegradable polymers [5,6] such as Starch [7], chitosan and lignin [8] from a renewable source of plants, animals, and microorganisms have been successfully used as coating materials.

Enzymatic degradation of hydrophilic biopolymers such as poly(vinyl alcohol) (PVA) and modified starch is given by Spiridon et al [9]. They reported that the degrading enzymes have a significant effect on biopolymer weight loss. Weng et al [10] studied the biodegradation behavior of modified starch in soil conditions. It was observed that time was reduced by the sample weight, oxygen was increased, and carbon was reduced in the soil environment. Starch/PLA/poly(hydroxyester-ether) bars were placed in soil to study the biodegradation [11] of these polymers. It is reported that the biodegradation is mainly caused by starch [12].

Many researchers [4] have reported the effect of enzymatic degradation of nutrient release profiles. However, there is no mathematical model to predict the nutrient release profiles by considering the enzymatic degradation coupled with diffusion. There are few models in the literature to discuss only the enzymatic degradation of biopolymers [13] based on first-order kinetics. The model has considered all the physical phenomena responsible for enzymatic degradation. However, the model considers only the degradation and while the nutrient release from CRF was not considered in the model. Mathematical models on the enzymatic degradation are given by [14–16]. These models successfully predicted the enzyme hydrolysis of a biopolymer. However, to execute these models, the Gel permeation chromatography (GPC) data is required from experiments. There is no model in the literature for the coupled study of nutrient release and enzymatic degradation.

Mathematical Models are seemingly divided into mechanistic and empirical models and are responsible for ensuring the synchronous supply of available nutrients with sequential plant requirements while designing the polymer-coated fertilizer. The nutrient release takes place after applying the controlled release fertiliser to soil and relies on it, the underlying physics, chemistry, and possible biological processes are described by theoretical models. Utilizing the in-depth CRF parameters, these models predict nutrient release from controlled-release fertilizer. However, in most of the cases, the difference between the release profile determined for a CRF population and the one expected for one single granule is significantly different.

The differences are created due to high variation within a CRF population, and this variation can mainly be seen in the distribution of granule radii and coating thickness. The change in the weight of individual CRF granules can be up to 38% [17]. In the case when the fertilizer granules are not sieved before coating, significant differences are generated in the coating thickness, the reason being the strong dependence of coating thickness distribution on the initial granule size distribution. A population of CRF granules, when compared to one single granule, is more often used in fertilizer release experiments or field conditions. Few researchers first established a theoretical model for a single CRF granule before scaling it to the CRF population by including the distribution of granule radii and coating thickness via population statistics [18]. However, the utilization of these models in practical applications is limited to complex population statistics.

The diffusion release model from polymer-coated fertilizer has been studied by Shaviv et al [19,20]. The model takes the non-Fickian diffusion model approach to model the nutrient release from CRF for a single and population of the controlled release fertilizer. The analytical solution can be utilized to study the nutrient release from CRF. The saturation and nutrient release from coated spherical shaped granules using the granules' contact areas with different soil is studied by Basu et al [21,22]. The model has also incorporated the effect of granule radius, diffusion coefficient, and contact area of the granule with soil. The model is based on the diffusion equation and solved using the explicit finite

difference scheme. Al-Zahrani [23] has also studied the diffusion-based model for nutrient release from controlled-release fertilizer. The model consists of analytical and numerical solutions do the diffusion equation.

The nutrient release is estimated by empirical models based on the observed relationships among nutrient release profiles and factors impacting their release. The development of these models is based on first-order kinetic relationships [24–26], two-stage linear relationships [27] or simplistic functions of time predicted urea release profiles from a CRF population depending on an artificial neural network (ANN) and unified extreme analysis, respectively [28].

There is no machine learning model in the literature to predict the nutrient release time from the diffusion coefficient, CoV of coating thickness, coating mass, surface hardness, and CoV of size distribution.

1.1. Enzymatic Degradation of Biopolymers

Enzymatic degradation of polymers is a complicated phenomenon. Polymer degradation depends on the arrangement of polymeric substrates and the active state of enzymes in the degradation sites. Different techniques of enzymatic degradation of polymers are explained by Banerjee et al [29].

An analytical model is developed by Azhari et al [30] considering the basic Michaelis-Menten kinetics. When a polymer comes in contact with degrading enzymes, the chain fragments of the polymer with i residues (S_i) are generated and consumed simultaneously.

1. The formation of residues (S_i) by enzyme hydrolysis of polymeric chains (S_y) via the complex (ES)_y is given below:

2. Generation and the decomposition of complexes ES_i between the enzymes and the residues are given below:

In the enzymatic hydrolysis of biopolymers in the soil, the reaction rate (k_3) remains constant throughout the reaction. Hence, the production of monomers in polymer as presented by [30] is given below:

$$\left(\frac{dC_1}{dt}\right)_p = \frac{k_3}{K_M} C_{eff} C_E \quad (1)$$

where $C_{eff} = \sum_{j=1}^N C_j$.

Hence by simplifying the Equation (1) we get the production of monomers in the polymer as explained in Equation (2).

$$\left(\frac{dC_1}{dt}\right)_p = \frac{k_3}{K_M} C_E \sum_{j=1}^N C_j \quad (2)$$

Equation (2) is further simplified to consider the concentration of all the enzymes (C_{ET}) available for enzymatic degradation of polymers and is given below:

$$C_E = \frac{1}{K_M} \frac{C_{ET}}{1 + \sum_{j=1}^N C_j} \quad (3)$$

The Equation (3) is simplified for concentration of polymeric drug chains in CRF (C_j) and is given in the form of differential equation first proposed by [30,31] such that:

$$R_E = \left(\frac{dC_1}{dt}\right)_p = \frac{k_3 C_{ET} \sum_{j=1}^N C_j}{K_M + \sum_{j=1}^N C_j} \quad (4)$$

$$\frac{dC_j}{dt} = \frac{k_3 C_{ET} C_j}{K_M + \sum_{j=1}^N C_j} + \frac{k_3 C_{ET} C_{j+1}}{K_M + \sum_{j=1}^N C_j} \quad (5)$$

To compute the term R_E , the N differential equation obtained from Equations (4) and (5) was been solved using Euler's integration method [32]. Subsequently, the solution is substituted in the numerical inversion algorithm for each time steps.

The M-M kinetic parameters of the three aliphatic polyesters utilizing the enzymatic hydrolysis with *Rhizopus delemar* lipase by kinetic Equation (6) was studied by Bikiaris et al. [33]. The kinetic constant (k_{-1}) reduced from 0.036, 0.028 and 0.009 day⁻¹ for poly(ethylene succinate), poly(propylene succinate) and poly(butylene succinate) (PBSu), respectively. Increasing the spacing between ester groups of these polymers also led to the rise in the susceptibility to enzymatic attack:

$$\theta = \frac{k_1 C_E}{k_1 C_E + k_{-1}} (1 - \exp(-(k_1 C_E + k_{-1}) t)) \quad (6)$$

where t represents the time, refers to the fraction of a substrate occupied by the ES complex, and the enzyme concentration is denoted by C_E .

2. Materials & Methods

2.1. Materials & Pre-Treatment

Substrate urea granules from PFK Sdn Bhd (Kedah-Malaysia) were sieved to obtain a specific size range as illustrated in Table 1.

Table 1. Size ranges of substrate particles.

Size Range	% Population
2.5–3.0 mm	3%
1.5–2.0 mm	60%
Beow 1.0 mm	37%

Granules of 1.5–2 mm size range were chosen for fluidized-bed coating. PVOH (Polyvinyl Alcohol-Cross-Linked Starch) (Purity > 99.9%) and citric acid (99.8%) were purchased from Merck®, Malaysia. Citric acid serves the purpose of a cross linker between starch and PVOH (Polyvinyl Alcohol-Cross-Linked Starch) that strengthens inter- and intra-molecular hydrogen bonding caused by OH- functional groups of both starch and PVOH [34,35]. Tapioca starch with a brand name Kapal ABC Malaysia, was purchased from TESCO, Malaysia. It was stored at −20 °C to avoid the possibility of any microbial attack.

2.2. Preparation of St-PVOH (Starch Based Polyvinyl Alcohol-Cross-Linked Starch) Solution

St-PVOH solution was prepared by dissolution of polyvinyl alcohol in distilled water at 90 °C with stirring by Teflon magnet for 45 min. Fully mixed aqueous solution of tapioca starch was introduced into PVOH solution and the stirring was continued for another 90 min at 85 °C. The temperature of resultant mixture was subsequently decreased to 30 °C. At this point, citric acid solution was added into the mixture. Agitation was continued for another 90 min and the final St-PVOH solution was allowed to cool down to room temperature.

2.3. Preparation of St-PVOH Coated Urea (St-PCU)

A rotary fluidized bed coater/granulator was used for the preparation of St-PVOH coated urea. Substrate urea granules (200 g) were introduced on the motor driven rotary plate. The granules were pre-dried in an air dryer to remove any traces of moisture until a constant weight of granules is achieved. The temperature of fluidized bed was monitored by number of thermocouples along the height of the column. Air from the room environment is suction driven through a filter and heater such that the filtered and heated air passes through the height of fluidized bed column and escapes through

the vent on top (refer to Figure 1). The substrate urea granules are fluidized when the dried hot air passes through the annular space between rotary plate and the column wall. A two-fluid nozzle serves the purpose of an atomizer. The high pressure air atomizes the coating solution that is introduced into the two fluid nozzle via a peristaltic pump. Spray coating starts when steady state temperature conditions are reached. The tangential spray orientation in the rotary fluidized bed coater facilitates the encapsulation of urea granules at a rapid pace with minimum spray loss on column walls. All the process and operational conditions are set before the spray coating starts. A digital controller is used to adjust and monitor the process conditions such as fluidizing air flow and temperature, atomizing air flow and temperature, spray rate and spray temperature etc. Spray is introduced intermittently to avoid agglomeration and possible defluidization. The spray supply is cut off and the fluidizing air supply is continued for 5–10 min for the coated granules to dry. This concludes the coating session.

Figure 1. Schematic arrangement of rotary fluidized bed equipment for St-PCU production [34].

2.4. Controlled Release Characteristics of St-PCU

Standard curve method is used to estimate the urea absorbance and subsequently, the release time of urea into distilled water. For this purpose, UV-Vis Spectrophotometer (developed by JASCO V-630, Japan) was used. Known mass of coated product was immersed in ultra-refined distilled water in a properly sealed glass beaker. The aliquots were stirred softly after regular time intervals and a known volume of it was taken out for absorbance measurement. The volume of liquid in beaker was made-up with the addition of equal volume of refined distilled water. The absorbance of light by the urea solution was measured three times at a wavelength of 500 nm and a mean value was used to determine urea concentration from standard curve.

2.5. Coating Uniformity of St-PCU

Coating uniformity was determined by the following three mechanisms:

1. By evaluating the coefficient of variance of film thickness
2. By evaluating the coefficient of variance of size distribution
3. By evaluating the change in coating mass deposited on the surface of granules

2.6. Coefficient of Variance of Coating Thickness

10 granules from each sample were randomly chosen and cut into two pieces with an extremely sharp knife after their immersion into liquid nitrogen. Each cross section was subjected to microscopic

analysis under the Field Emission Scanning Electron Microscope developed by Zeiss Supra 55 VP® (Germany). The coating film thickness was marked from 20 equally-spaced locations on the cross-section and mean thickness was determined. All the data points were noted and the coefficient of variance of coating film thickness was reported as a measure of the coating uniformity.

2.7. Coating Mass Variance of St-PCU

Local variation of coating mass can also be used as a measure of coating uniformity. In this case, 50 randomly chosen coated granules were subjected to urea dissolution in distilled water. After the complete dissolution of urea, the coating shells were carefully sieved, dried, and weighed to report the mean coating mass received by each granule. The change in mean coating mass for different samples is reported in terms of the change in process conditions.

2.8. Coefficient of Variance of Size Distribution of St-PCU

Coefficient of variance of size distribution of the coated product is another measure of the coating uniformity. Lower the size distribution of the overall population, better the coating quality and vice versa. In this case, we used ERWEKA TBH325TD tester to evaluate the size distribution. 100 granules from each coated sample were randomly chosen and their diameters were determined using the aforesaid tester. The coefficient of variance of particle diameter (size) was reported as a measure of the coating uniformity.

2.9. Experimental Design & Process Optimization

Central Composite Rotatable Design (CCRD) was used to perform the Analysis of Variance (ANOVA) of the obtained results. For this purpose, we used Design Expert 8.0® to generate the experimental matrix and statistical analysis of the results achieved. Before using the CCRD technique, several trial runs were performed to investigate the minimum and maximum values of the process variables which are given in Table 2.

Table 2. Minimum & maximum values of process variables via trial runs.

Sr	Process Variables	Min Value	Max Value
1	Atomizing air pressure (Bar)	0.05	0.4
2	Fluidizing gas temperature (°C)	50	120
3	Spray rate (RPM)	0.5	5.0
4	Spray temperature (°C)	70	100
5	Coating time (min)	30	150

The CCD approach generated 50 experimental runs for these five process variables with 8 central points which are also called as repeated runs or replicates and are helpful for the process optimization. The experimental data utilized in the machine learning model development is presented in the following Table 3.

Table 3. Experimental data utilized to develop machine learning model.

Rel.Time (RT)	Diff. Coeff	Coat.Mass	CV Siz Dist. (SD)	Surf.Hard. (SH)	CV Coat.Thick. (CT)
1.833	7.54	26.184	8.08	58.9	12.185
1.667	6.26	23.803	7.84	48.9	18.56
2.278	7.78	32.531	6.11	62.78	29.629
9.111	1.05	130.127	4.88	58.1	12.156
5.222	4.0710	74.584	6.47	68.95	14.285
5.889	5.513	84.105	10.26	70.7	16.571
2.611	1.260	37.292	6.873	81.8	16.123
17.5	9.768	249.9	3.88	89.2	13.317
1.944	1.704	27.771	8.824	54.25	14.907
0.943	4.22	13.489	7.194	60.1	34.585
0.917	1.30	13.092	9.957	53.7	27.167
2.666	1.111	38.085	8.807	55.7	17.85
2	7.7015	28.564	6.62	80.5	18.69
2.611	1.877	37.292	5.338	68.5	34.521
6.666	1.025	95.215	5.852	89.36	21.712
2.556	2.49	36.49	3.41	59.9	14.167
1.833	2.86	26.18	6.296	68.4	22.372
2.5	8.571	35.70	6.32	72.08	18.713
16.167	9.76	230.89	4.077	82.6	13.095
13.667	7.23	195.19	5.53	88.75	13.882
2.778	2.13	39.673	7.527	69.12	32.088
17.33	1.17	247.55	3.782	81.02	13.48
2.166	8.70	30.945	5.264	76.2	27.491
15.333	8.83	218.994	6.24	76.3	12.794
2.388	6.330	34.119	7.49	56.6	24.087
22.667	9.24	323.73	2.854	101.23	11.590
4.444	1.6	63.475	6.41	56.5	14.51
16.83	9.63	240.417	4.227	78.3	12.92
1	4.619	14.282	5.66	73.2	27.12
11.333	7.171	161.86	4.846	79.5	13.92
3.778	5.16	53.9	7.58	65.23	16.256
2.166	4.526	30.945	11.862	60.25	12.9
6.33	1.19	90.45	6.31	84.36	22.85
14.667	2.77	209.47	7.24	84.85	13.682
0.55	4.350	7.934	8.361	49.63	31.152
0.639	5.039	9.125	9.845	58.98	23.51
16.667	1.176	238.0	4.1	93.26	12.683
8.6669	1.26	123.779	5.21	87.21	21.251
12.167	3.21	173.767	6.92	85.6	12.39
0.83	4.54	11.9	9.2	53.6	19.9
4.6	1.8	66.6	4.8	71.25	20.875
1.083	8.7	15.472	7.2	56.3	29.659
15.833	9.3	226.13	5.0	85.2	13.333
15	8.5	214.233	7.92	88.69	12.583
3.33	2.40	47.60	6.0	90.9	22.035
1.306	5.02	18.641	8.66	48.63	32.45
8.11	1.0	115.845	6.875	69.31	26.48
1.778	4.634	25.39	12.581	47.21	12.895
1.25	3.0	17.8	9.27	61.58	23.1
14.167	8.2	202.33	6.07	77.6	13.5

3. Gaussian Process Regression (GPR) Based Machine Learning

The Gaussian process is a type of supervised machine learning method used for probabilistic classification and regression problems. The powerful ability of the algorithm to enable inference tractability (by supplement of convenient properties of Gaussian Distribution). Yu et al. 2017 [36] explain that there is possibly two basis of the algorithm which are parametric regression and Bayesian

regression. Parametric regression determines the suitable parameter set that can show mappings such as neural network and polynomial regression. Over-fitting is the main problem of this process as the algorithm focuses on minimizing the error and disregards the generalization of the model. This may work on training sets but not for other data sets [36]. The second one is the Bayesian Regression. This process compensates the problems caused by the first process by defining a single function distribution and another possible function has a prior probability. GPR is a good regression method for problems that involve small samples, high-dimension processes, and non-linear problems. To control the accuracy of the algorithm, Kernel functions are applied to provide a data manipulating medium for data projection in a higher-dimensional space. This helps to make regression easier and more efficient for model building. Multiple functions of Kernel co-variance is tested and later compared with other machine learning method. The research successfully proves the ability of GPR to generate a model in a shorter time and less data points [37].

4. Results and Discussion

A theoretical model was utilized to provide qualitative justification for the variation of the nutrient/urea release profile with various controlled release parameters mentioned in the experimental data acquisition section and the variation of nutrient release with diffusion coefficient is presented in the following Figure 2.

Figure 2. Cumulative nutrient release time with diffusion coefficient.

However, its quantitative explanation, on the consideration of biodegradation of biopolymer coating was not sufficient. The reason being the inconsistent diffusion coefficient during the entire release process. Machine learning-based modeling can be an alternative approach that offers traditional mathematical models for the estimation of nitrate release by considering the different process parameters of biopolymer coated CRF production. Testing results showed a high similarity between the estimated release profiles and those obtained from the experimental results.

Shen et al. [38] estimated the nutrient release profiles from a CRF population by utilizing a self-established mathematical model while excluding the variation within a population and got R^2 and RMSE values of 0.768 and 3.48, respectively. Shaviv et al. [19] included the distribution of granule radii and coating thickness to scale a self-established mathematical model to the CRF population.

In another study, both the distributions of the radii and coating thickness were considered to be normal distributions in this statistical model. The RMSE values received for polyurethane (PULC) and modified polyolefin (MPO) coated fertilizers were 3.20% and 3.80%, respectively. The study concluded that errors may occur due to the deviation of the real size distribution from the normal distribution [39].

GPR model offers better accuracy in the estimation of nutrient release from biopolymers coated CRF and is simpler to use when compared to the theoretical model. Although this application requires further improvement, it is useful in the optimization of controlled-release parameters for a given release rate while designing the desired PCF and benefit the PCF industry.

In this model, the inputs variables utilized were diffusion coefficient, CoV of coating thickness, coating mass, surface hardness, CoV of size distribution. Hence, resulting in considerable improvement in the prediction capabilities of the GPR model (R^2 and RMSE values were 0.999 and 0.0034).

The GPR model is optimized in terms of Kernel selection by varying it with different kernels and recording the R^2 and RMSE of each in the following Table 4.

Table 4. Effect of Kernel function on developed machine learning model.

Sr	Kernel Function	RMSE	R^2
1	Rational Quadratic GPR	0.003	1
2	Squared Exponential GPR	0.003	1
3	Matern/GPR	0.003	0.98
4	Exponential GPR	0.98	0.96

From the Table 4 it can be concluded that Exponential GPR kernel lacks behind the other kernel's in terms of accuracy and error analysis. Furthermore, as a machine learning model, the input data of the machine learning model can be easily compared to the diffusion coefficient, co-variance of coating thickness, coating mass. Hence, the GPR model is powerful in modeling nutrient release due to its simplicity and accuracy. Figure 3 represents the prediction accuracy of the GPR model. The developed model has the r squared of 1 with a mean square error of 0.3.

CRF product is needed and utilized as inputs during the usage of the GPR model to estimate the nutrient release from biopolymer coated fertilizer, diffusion coefficient, coefficient of-variance of coating thickness, coating mass thickness, surface hardness, coefficient of variance of size distribution and surface hardness. Also, the GPR model will be directly utilized to get the cumulative nutrient/urea release time of unknown products the results of the model development are presented in Figure 3. The optimization of the GPR model with different kernels is presented in Figure 4. For the usage of the GPR model in the case of other types of biopolymer-coated CRF, the inputs and outputs must be obtained for this kind of product. Also, the establishment of the calibration model and testing the prediction must be done. Until the prediction effect is satisfied, the GPR model will then predict the cumulative release of unknown products.

The [28] develops the generalized regression neural network (GRNN) model for polymer-coated controlled-release fertilizer. The model has shown a greater accuracy with 0.99 r squared value. The model inputs are membrane thickness, temperature, granule radius, and saturated concentration of the nutrients. The developed model in this study, and the GRNN model by Du et al [28] has shown that artificial intelligence modeling can be useful in designing and developing modern controlled-release fertilizer.

Figure 3. Comparison of experimental and machine learning model results of release time.

Figure 4. Optimization of the GPR model with maximum and minimum mean square error with different kernels.

5. Conclusions

A machine learning-based model based on Gaussian process regression (GPR) is developed to predict the nutrient release from a biopolymer coated controlled-release fertilizer that undergoes enzymatic and microbial degradation concurrently. The kernel optimization of the GPR is also proposed in this study. The optimized model has good predictability with an R^2 value of 1 and RMSE value of 0.003 by considering the inputs of diffusion coefficient, coefficient of variance of coating thickness, coating mass thickness, coefficient of variance of size distribution and surface hardness. The model results are compared with the experimental results and the predicted results are in good agreement with the experimental results. The experimental results are used from a study in which polyvinyl alcohol-modified starch (crosslinked with citric acid) is used as a coating material for the production of coated urea granules in a fluidized bed. The model can be successfully implemented for designing new controlled-release fertilizers based on the other biodegradable polymers.

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Abbreviations

The following abbreviations are used in this manuscript:

GPR Gaussian Process Regression
CRF Controlled Release Fertilizer
SRF Slow Release Fertilizer

References

1. United Nations. *World Population Prospects*; Technical Report; United Nations: New York, NY, USA, 2015.
2. Trenkel, M.E. *Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture*; International Fertilizer Industry Association: Paris, France, 2010.
3. Salimi, M.; Motamedi, E.; Motesharezedeh, B.; Hosseini, H.M.; Alikhani, H.A. Starch-g-poly(acrylic acid-co-acrylamide) composites reinforced with natural char nanoparticles toward environmentally benign slow-release urea fertilizers. *J. Environ. Chem. Eng.* **2020**, *8*, 103765. [[CrossRef](#)]
4. Majeed, Z.; Ramli, N.K.; Mansor, N.; Man, Z. A comprehensive review on biodegradable polymers and their blends used in controlled-release fertilizer processes. *Rev. Chem. Eng.* **2015**, *31*, 69–95. [[CrossRef](#)]
5. Phang, S.W.; Sin, L.T.; Bee, S.T.; Tee, T.T. Release kinetic model of nitrogen released encapsulated in starch-alginate controlled released urea: Diffusion and its decay release. In *AIP Conference Proceedings*; AIP Publishing LLC: Melville, NY, USA, 2020; p. 040006. [[CrossRef](#)]
6. Fertahi, S.; Bertrand, I.; Ilsouk, M.; Oukarroum, A.; Amjoud, M.; Zeroual, Y.; Barakat, A. Impact of Plasticizers on Lignin–Carrageenan Formulation Properties and on Phosphorus Release from a Coated Triple Superphosphate Fertilizer. *Ind. Eng. Chem. Res.* **2020**, *59*, 14172–14179. [[CrossRef](#)]
7. Naz, M.Y.; Sulaiman, S.A. Slow release coating remedy for nitrogen loss from conventional urea: A review. *J. Control. Release* **2016**, *225*, 109–120. [[CrossRef](#)] [[PubMed](#)]
8. Majeed, Z.; Mansor, N.; Man, Z.; Wahid, S.A. Lignin reinforcement of urea-crosslinked starch films for reduction of starch biodegradability to improve slow nitrogen release properties under natural aerobic soil condition. *e-Polymers* **2016**, *16*, 159–170. [[CrossRef](#)]
9. Spiridon, I.; Popescu, M.C.; Bodărlău, R.; Vasile, C. Enzymatic degradation of some nanocomposites of poly(vinyl alcohol) with starch. *Polym. Degrad. Stab.* **2008**, *93*, 1884–1890. [[CrossRef](#)]
10. Weng, Y.X.; Wang, L.; Zhang, M.; Wang, X.L.; Wang, Y.Z. Biodegradation behavior of P(3HB,4HB)/PLA blends in real soil environments. *Polym. Test.* **2013**, *32*, 60–70. [[CrossRef](#)]

11. Shogren, R.; Doane, W.; Garlotta, D.; Lawton, J.; Willett, J. Biodegradation of starch/polylactic acid/poly(hydroxyester-ether) composite bars in soil. *Polym. Degrad. Stab.* **2003**, *79*, 405–411. [\[CrossRef\]](#)
12. Tomasik, P.; Horton, D. *Enzymatic Conversions of Starch*, 1st ed.; Elsevier Inc.: Amsterdam, The Netherlands, 2012; Volum 68, pp. 59–436. [\[CrossRef\]](#)
13. Tzafriri, A.R. Mathematical modeling of diffusion-mediated release from bulk degrading matrices. *J. Control. Release* **2000**, *63*, 69–79. [\[CrossRef\]](#)
14. Watanabe, M.; Kawai, F.; Shibata, M.; Yokoyama, S.; Sudate, Y. Computational method for analysis of polyethylene biodegradation. *J. Comput. Appl. Math* **2003**, *161*, 133–144. [\[CrossRef\]](#)
15. Watanabe, M.; Kawai, F. Simulation for microbial depolymerization processes of polyethylene glycol. *WIT Trans. Inf. Commun. Technol.* **2014**, *53*, 97–107. [\[CrossRef\]](#)
16. Watanabe, M.; Kawai, F. Solutions of inverse problems for biodegradation of xenobiotic polymers. In *AIP Conference Proceedings*; AIP Publishing LLC: Melville, NY, USA, 2016; p. 050019. [\[CrossRef\]](#)
17. Takahashi, S.; Ono, S.I. Nitrogen release from polyolefin-coated urea with attention to individual weights. *Nutr. Cycl. Agroecosystems* **1996**, *46*, 153–156. [\[CrossRef\]](#)
18. Zaidel, E. *Models of Controlled Release of Fertilisers*; Research Thesis; Agricultural Engineering Technion-IIT: Haifa, Israel, 1996.
19. Shaviv, A.; Raban, S.; Zaidel, E. Modeling controlled nutrient release from a population of polymer coated fertilizers: Statistically based model for diffusion release. *Environ. Sci. Technol.* **2003**, *37*, 2257–2261. [\[CrossRef\]](#)
20. Shaviv, A.; Raban, S.; Zaidel, E. Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. *Environ. Sci. Technol.* **2003**, *37*, 2251–2256. [\[CrossRef\]](#)
21. Basu, S.; Kumar, N. Mathematical model and computer simulation for release of nutrients from coated fertilizer granules. *Math. Comput. Simul.* **2008**, *79*, 634–646. [\[CrossRef\]](#)
22. Basu, S.K.; Kumar, N.; Srivastava, J.P. Modeling NPK release from spherically coated fertilizer granules. *Simul. Model. Pract. Theory* **2010**, *18*, 820–835. [\[CrossRef\]](#)
23. Al-Zahrani, S.M. Controlled-release of fertilizers: Modelling and simulation. *Int. J. Eng. Sci.* **1999**, *37*, 1299–1307. [\[CrossRef\]](#)
24. Irfan, S.A.; Razali, R.; Shaari, K.Z.K.; Mansor, N. Modelling and simulations of controlled release fertilizer. In *AIP Conference Proceedings*; AIP Publishing LLC: Melville, NY, USA, 2016; p. 080025. [\[CrossRef\]](#)
25. Irfan, S.; Razali, R.; KuShaari, K.; Mansor, N. Reaction-Multi Diffusion Model for Nutrient Release and Autocatalytic Degradation of PLA-Coated Controlled-Release Fertilizer. *Polymers* **2017**, *9*, 111. [\[CrossRef\]](#)
26. Irfan, S.A.; Razali, R.; KuShaari, K.; Mansor, N.; Azeem, B.; Ford Versypt, A.N. A review of mathematical modeling and simulation of controlled-release fertilizers. *J. Control. Release* **2018**, *271*, 45–54. [\[CrossRef\]](#)
27. Jarrell, W.M.; Pettygrove, G.S.; Boersma, L. Characterization of the thickness and uniformity of the coatings of sulfur-coated urea. *Soil Sci. Soc. Am. J.* **1979**, *43*, 602. [\[CrossRef\]](#)
28. Du, C.; Tang, D.; Zhou, J.; Wang, H.; Shaviv, A. Prediction of nitrate release from polymer-coated fertilizers using an artificial neural network model. *Biosyst. Eng.* **2008**, *99*, 478–486. [\[CrossRef\]](#)
29. Banerjee, A.; Chatterjee, K.; Madras, G. Enzymatic degradation of polymers: A brief review. *Mater. Sci. Technol.* **2014**, *30*, 567–573. [\[CrossRef\]](#)
30. Azhari, R.; Lotan, N. Enzymic hydrolysis of biopolymers via single-scission attack pathways: A unified kinetic model. *J. Mater. Sci. Mater. Med.* **1991**, *2*, 9–18. [\[CrossRef\]](#)
31. Gold, T.; Azhari, R.; Lotan, N. Enzyme-Promoted Degradation of Polymeric Matrices for Controlled Drug Delivery: Analytical Model and Numerical Simulations. In *Degradation of Implant Materials*; Eliaz, N., Ed.; Springer: New York, NY, USA, 2012; Chapter 8, pp. 173–194. [\[CrossRef\]](#)
32. LeVeque, R.J. *Finite Difference Methods for Ordinary and Partial Differential Equations*; SIAM: Philadelphia, PA, USA, 2008; pp. 1–356. [\[CrossRef\]](#)
33. Bikiaris, D.N.; Papageorgiou, G.Z.; Achilias, D.S.; Dimitris, S. Synthesis and comparative biodegradability studies of three poly (alkylene succinate) s. *Polym. Degrad. Stab.* **2006**, *91*, 31–43. [\[CrossRef\]](#)
34. Azeem, B.; KuShaari, K.; Man, Z.; Irfan, S.; Trinh, T. Tumbling fluidized-bed process parameters affecting quality of biopolymer coating on surface of pristine urea particles. *Powder Technol.* **2017**, *320*, 714–725. [\[CrossRef\]](#)

35. Azeem, B.; KuShaari, K.; Man, Z.; Irfan, S.A. Parametric study of tumbling fluidized bed to evaluate nitrogen release characteristics of biopolymer-coated controlled release urea. *Chem. Eng. Commun.* **2018**, *205*, 1397–1414. [[CrossRef](#)]
36. Yu, H.; Rezaee, R.; Wang, Z.; Han, T.; Zhang, Y.; Arif, M.; Johnson, L. A new method for TOC estimation in tight shale gas reservoirs. *Int. J. Coal Geol.* **2017**, *179*, 269–277. [[CrossRef](#)]
37. Sun, S.; Sun, Y.; Sun, C.; Liu, Z.; Dong, N. Methods of calculating total organic carbon from well logs and its application on rock's properties analysis. *GeoConvention 2013 Integr.* **2013**, *41372*, 7.
38. Shen, Y.Z.; Du, C.W.; Zhou, J.M.; Ma, F. Modeling nutrient release from swelling polymer-coated urea. *Appl. Eng. Agric.* **2015**, *31*, 247–254. [[CrossRef](#)]
39. Shen, Y.Z.; Du, C.W.; Zhou, J.M.; Ma, F. Release profile predictions of controlled release fertilisers: Least Squares Support Vector Machine. *Biosyst. Eng.* **2018**, *31*, 67–74. [[CrossRef](#)]

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