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Release Kinetic Model of Nitrogen Released Encapsulated in Starch-Alginate Controlled Released Urea: Diffusion and Its Decay Release

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Abstract. Controlled released urea (CRU) encapsulated in starch-alginate (St-Alg) cross-linked with calcium chloride was investigated as a supplement of N-nutrient for the use in agriculture nursery. The urea concentration was determined with ultraviolet/visible light absorption spectrophotometer (UV/VIS). The urea release data was fitted and compared with 3 empirical exponential equations models to support the interpretation and comprehension of the release mechanisms. The release kinetic for St-Alg CRU beads was found to have good Ritger-Peppas model fitting at R^2 value more than 0.99, which suggested that the release behaviour of urea in St-Alg matrix consists of three stages: i. an extremely low diffusion exponential (*n*) value, indicating an initial rapid release of urea attributed to the high surface's porosity of St-Alg beads, that allowing an instantaneous water penetration into the matrix that dissolved and release the soluble content, which can be observed in the ; ii. a period of linear release when the solution reaches an equilibrium while the total volume of the polymer matrix remains almost constant; and iii. an extremely high *n* value (>0.86) indicating the rapid "decaying release" of urea caused by the decaying of the hydrophilic polymer matrix.

INTRODUCTION

Fertilizers are generally referred to the three main nutrients: nitrogen (N), phosphorus expressed as phosphate (P_2O_5), and potassium expressed as potash (K_2O). The demand of fertilizers are expected to continually expand in the next few decades due to the population growth and the needs for food. In the recent report released by International Fertilizer Association, the global fertilizer consumption reached 187 million tonnes (Mt) of nutrients for the period of 2017/18 [1]. Between 2017 and 2022, global nitrogen supply is expected to expand by an average of 0.6% per annum with an annual increment of 1.2% in demand, where urea itself accounted for 55% of the nitrogen production in year 2017 [1]. It is known that nitrogen (N) is often classified as the crops yield limiting nutrient, where plant growth is highly dependence on N availability [2]. However, it was found that the overall efficiency of N utilisation in agriculture is rather low, often results in between 30 to 50% [3]. About 20 to 70% of conventionally applied N fertilizers are lost to the environment through nitrification leaching or ammonia volatilization [4], which is economically inefficient and it creates environmental pollution. One solution involves the usage of controlled-release fertilizers (CRFs). CRF are designed to improve crops yield and reducing pollution caused by the hazardous emission such as ammonia, nitrite and nitrate from current fertilizer application [5].

One of the most important and challenging areas in controlled released technology is the prediction of release behaviour of the active ingredient as a function of time using mathematical models [6–11]. Kinetic study of the fertilizer release in a controlled environment is crucial to in predicting the transportation of nutrients within the matrix and its degradation of the polymer, which the information is important for the plantation management in fertilizer scheduling and costing. In order to identify a release mechanism, experimental data of statistical significance are

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compared and fitted into series of theoretical model. Therefore, it is clear that only a combination of accurate and previse data with models accurately depicting the physical situation provides an insight to the actual mechanism of released. Shaviv et al. [13] proposed a comprehensive model describing the complex and "non-Fickian" nutrient release from hydrophobic-material coated CRF, in which, consists of three release stages: an initial stage where no release was observed, but a lag period where water penetration into the matrix for nutrient dissolution, followed by a constant steady state release, and finally, a stage of graduate decay of release.

Most suggested models are based on diffusion Eq. 10 and Eq. 14–18. The Higuchi model assumes that Fickian diffusion is the predominant release mechanism [6], as shown:

$$\frac{M_t}{M_\infty} = k \times t^{0.5} \tag{1}$$

where M_t/M_∞ is the fraction of urea release, k is the release rate kinetic constant, t is the release time.

While the Higuchi equation addressed important aspects of active ingredient transportation and release mechanism, mainly used in pharmaceutical drug transport, it has been studied and modified by incorporating other factors such as diffusion controlled release [19], swelling controlled [15,16], matrix dissolution and diffusion release simultaneously [17] and many more. Ritger-Peppas model [15] suggested the hydrophilips matrix swelling release mechanism via the model:

$$\frac{M_t}{M_\infty} = k \times t^n \tag{2}$$

where M_t/M_∞ is the fraction of urea release, k is the release rate kinetic constant, t is the release time and n is the diffusion exponent for urea release. For film material, the diffusion exponent, $n = 0.50$ indicates a Fickian diffusion mechanism, that occurs by the usual molecular diffusion due to a chemical potential gradient [15]. $n = 1.0$ indicates a case II transport phenomenon, where the transport mechanism associated with two basic parameters: the diffusivity of the urea soluble, and the viscous flow rate of the glassy polymer [20]. Whereas for values in between $0.5 < n < 1.0$ are the superposition of both phenomena (anomalous transport) [15].

Another model was proposed by Peppas and Sahlin [17] that incorporate both parameters in case II transport phenomenon, the proposed model are as shown:

$$\frac{M_t}{M_\infty} = k_1 \times t^n + k_2 \times t^{2n} \tag{3}$$

where M_t/M_∞ is the fraction of urea release, k_1 is the diffusion constant, k_2 is the dissolving-erosion constant of the polymer material, t is the release time and n is the diffusion exponent for urea release. The first (right-hand side) terms indicates the cumulative release by diffusion, or so-called Fickian contribution, and the second (left-hand side) terms being the Case II relaxational contribution, indicating the cumulative release by dissolution of the polymer in water.

The above three classical equations derived from the concepts of Fickian diffusion, swelling and dissolution of matrix to predict the release behaviour of the active ingredient, mainly used in controlled released kinetic study for drugs. However, the objective of this research was to utilize these release kinetics concepts to describe the release pattern of fertilizers encapsulated in starch-alginate polymer matrix, in a controlled environment, in order to understand the transport phenomena of the nutrients within the matrix.

METHODOLOGY

Materials

Analytical grade of Sodium Alginate C.P., Calcium Chloride anhydrous granular C.P., and Urea were obtained from R&M Chemical, UK; whereas food grade cassava starch, brand Kapal ABC, manufactured in Thailand, was purchased off the shelf from grocery shop in Malaysia.

Preparation of hydrogel controlled-released urea

A defined amount of starch, alginate and urea was mixed in 25 mL distilled water as discussed in the previous paper presented by the authors [21] with slight modification in processes to due to different encapsulated active ingredient. The solution was heated up and stirred constantly at 600 RPM using a hot plate magnetic stirrer (Thermos Scientific MSH-300) for 15 – 30 min to achieve homogenous state. Cross-linking solution was prepared by dissolving $CaCl_2$ in 100 mL of distilled water. This was followed by the dripping of starch-alginate-urea mixture using a 2-mm diameter syringe into $CaCl_2$ solution for crosslinking action to occur. The formed starch-alginate-urea (St-Alg-U) beads were rinsed with distilled water, filtered using 200-mesh screen. The beads were dried in the natural convection oven (Memmert UN75) at 70°C overnight. Beads of different starch, alginate contents were prepared in different concentration of crosslinker. Total of 16 formulations divided into three categories: variation of alginate and Urea as shown in TABLE 1.

TABLE 1. St-Alg-Urea hydrogel beads formulation

Samples	Starch (phr)	Urea (phr)	Alginate (phr)
S1	100	50	5
S2	100	50	10
S3	100	50	15
S4	100	50	20
S5	100	100	5
S6	100	100	10
S7	100	100	15
S8	100	100	20
S9	100	150	5
S10	100	150	10
S11	100	150	15
S12	100	150	20
S13	100	200	5
S14	100	200	10
S15	100	200	15
S16	100	200	20

Urea release analysis and the release kinetic

1.5 g of the dried samples were added into 50 ml of distilled water in centrifuge tube. 3.5 ml of solution were sampled at interval of 1 hour, 2 hours, 4 hours, 8 hours, 24 hours, 2 days, 3 days, 1 week, 2 week, and 3 week till 8 week. At each sampling, 3.5 ml distilled water were added back to the solution in order to maintain the liquid at a constant volume. The urea content (C) was measured by ultraviolet / visible (UV/VIS) light absorption spectrophotometer (Thermo Scientific™ GENESYS 10S) at 210 nm wavelength, calculated using Eq. (4), derived from the calibration curve with a R^2 value of 0.999.

$$C = 19.317\,A + 0.4954 \tag{4}$$

where C is the urea concentration, A is the the absorbance value from UV/VIS Spectrophotometer.

The mechanism of the urea release from the polymer matrix was investigated by fitting several release kinetic models on urea release % versus time data. A non-regression analysis using Microsoft® Excel 2016 Solver Add-in was performed. Three classic empirical diffusion models were selected (Eq (1) - (3)): the Higuchi, Ritger-Peppas and Peppas-Sahlin double-exponent models to analyse the urea release kinetic; calculated as the ratio of cumulative amounts of urea release at time t (M_t), over total amount released at infinite time (M_∞) for each formulation.

The surface morphology of the samples before and after urea release analysis were scanned through a scanning electron microscope (SEM, JEOL JSM-5900, Japan), under the magnification range from 60x to 500x.

RESULT AND DISCUSSION

Fig.1 shows the cumulative observation for urea release from St-Alg-U beads for a period of two months, together with its statistical analysis in TABLE 2**.** The results shows that almost all urea encapsulated within the starch-alginate matrix was completed released within one month or a maximum period of 6 weeks, hence the variance analysis (TABLE 2) was only conducted for the release within 24 hours and one month (28 days). The interaction of alginate amount and urea contents in the matrix significantly affects the urea release behaviour, with the *P-value* less than 0.05. The release behaviour observed in Fig. 2 suggested that the release behaviour of urea in St-Alg matrix consists of three stages: i. an initial rapid release of urea up to nearly 40% within the first week, potentially due to the encapsulation matrix's surface morphology; ii. a period of linear release when the solution reaches an equilibrium while the total volume of the polymer matrix remains almost constant; and iii. the rapid "decaying release" due to the hydrophilic polymer matrix started to dissolved in water and resulted in an immediate release of all urea encapsulated at the end of one month period. The result of the current data is completely opposing the proposed model by Shaviv et al.[12], where the researchers suggested that the three phases of release involved a slow gradual starts where no release was even observed during the first phase, attributed to slow water penetration into the matrix, followed by a linear release and lastly a slower release due to reduction of the nutrients in the matrix. However, this was not the case for the current research as a result of the water affiliation nature in starch-base polymer.

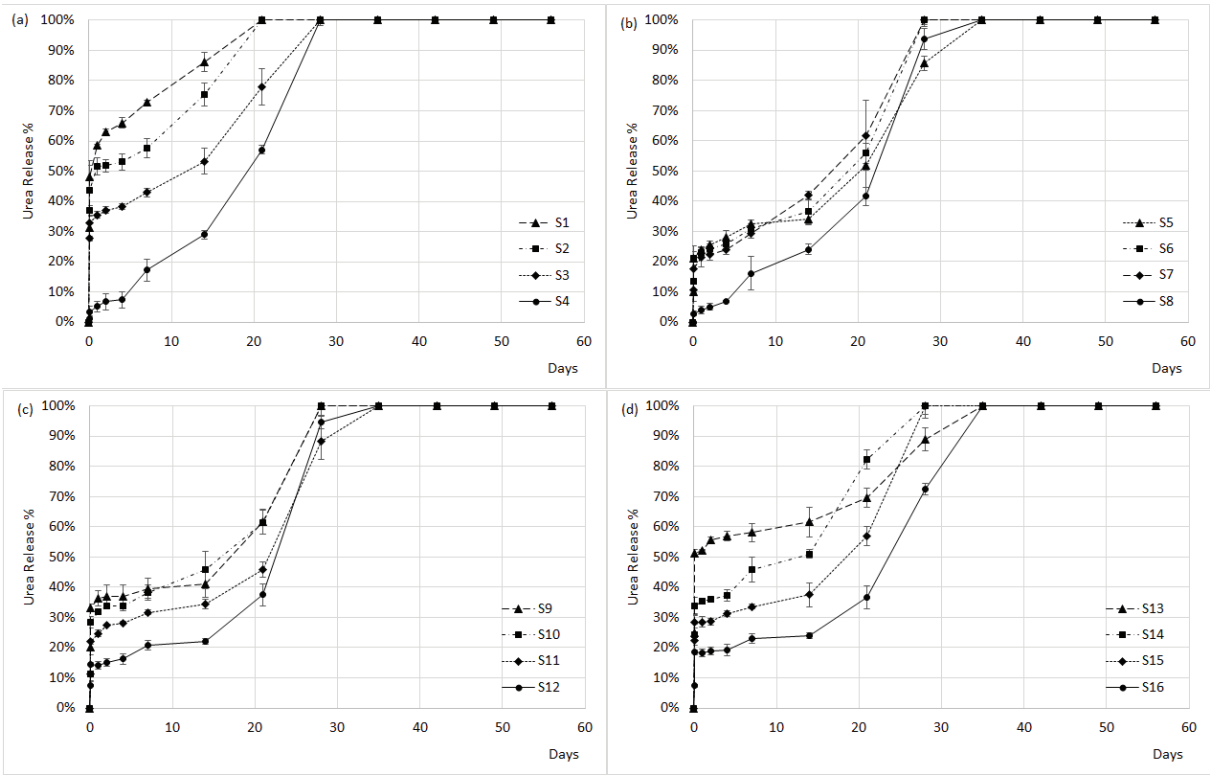

FIGURE 1. Two-months observation on urea release % in distilled water for starch-alginate urea beads at (a) 50 phr, (b) 100 phr, (c) 150 phr and (d) 200 phr urea encapsulated.

TABLE 2. Two-ways ANOVA analysis for urea release % in water for 24 hours and 28 days

Source of Variation	SS	df	MS	F	P-value	F crit
24 hrs release						
Alginate	0.3709	3	0.1236	444.67	3.76E-26	2.901
Urea	0.1590	3	0.0530	190.55	1.75E-20	2.901
Interaction	0.1182	9	0.0131	47.23	5.83E-16	2.189
Within	0.0089	32	0.0003			
Total	0.6570	47				
28 days release						
Alginate	0.4408	3	0.1469	17.64	6.13E-07	2.901
Urea	1.1217	3	0.3739	44.89	1.43E-11	2.901
Interaction	0.2887	9	0.0321	3.85	0.002177	2.189
Within	0.2666	32	0.0083			
Total	2.1179	47				

In order to understand the release behaviour of urea in the St-Alg matrix, it is important to study the release kinetic of the samples. Release kinetics model in TABLE 3 confirmed that the urea release from the St-Alg matrix was different from the analysis gathered for St-PVA CRU.

Higuchi model empirical equation was developed based on a few hypothesis that [6,8]: i. the solubility in the matrix in much lower than the initial solute concentration in the matrix; ii. the diffusion process or pathway is one dimensional; iii. the polymer swelling and dissolution are negligible and iv. the diffusivity is constant. However, the poor R^2 value obtained from Higuchi model, indicating the urea release kinetic did not follow the perfect Fickian's diffusion transportation phenomenon. It was clear that the release of urea was governed by other factors such as polymer swelling and dissolution, in which, was not reflected in this particular model that was in agreement with the finding from Siepmann and Peppas[8]. In all the previous research done by Peppas and his team on drug release behaviour by swellable polymer, they stated that the release phenomenon from swellable systems often disagree with the Higuchi model or the Fickian's behaviour, but consist of both diffusion of solute and relaxational swelling of the sample [8,14–17,19].

Ritger and Peppas [16] introduced a simple power law model that explained the mixed release mechanism which linked to multiple factors such as swelling, dissolution, matrix porosity and the solute release rate in swelling systems. In this model, four different release environments were suggested, referring to its diffusion exponent (n) values. Particularly for sphere samples, n value at 0.43, demonstrated a perfect Fickian diffusion, where urea diffusion occurred due to the chemical potential gradients. In the condition when the n values is larger than 0.86, a non-Fickian diffusion, Case II transport mechanism is observed, where the diffusion behaviour is dependence to the combination of several factors, including but not limited to polymer dissolution, swelling, as well as mechanical properties of the polymers [22]. Later, the Ritger-Peppas model was further developed by Peppas and Sahlin (1989) into a semi-empirical model to analyse the solute release from swellable polymer that include both diffusional and a relaxational component. However, from the non-regression fitting data as shown in TABLE 3, it was found that the dissolving-erosion constant of the polymer material, k_2, was very small, and it is negligible. Therefore, the Peppas-Sahlin model was found identical to the Ritger-Peppas model. With this finding, the model discussion from this point onwards for St-Alg CRU is focused on the release kinetic provided by Ritger-Peppas model.

Of all the 16 formulations for St-Alg CRU, 15 formulations gave a R^2 of 0.99, demonstrated the suitability of the selected model that explain the release mechanism of the CRU. As mentioned earlier, it was observed that there were three release stages in all the samples. During the first five to seven days of release period (phase I), the estimated the diffusion exponent, n value was extremely small, indicating the release during the first seven days was not of Fickian diffusion. Referring to the surface morphology (SEM image) of the sample shown in Fig. 2 (a) and (b), the surface of

the fresh St-Alg CRU bead was porous and the porosity increases after a 24-hours dissolution test in distilled water (Fig. 2 (c) and (d)). The high porosity of the polymer surface may have contributed to the extreme low *n* value (less than 0.3) in the Ritger-Peppas release kinetic model, as these pores on the polymer surface had allowed an instantaneous water penetration into the matrix, dissolving the soluble content and release them, which was similar to the reports from previous researchers, that low *n* value on sulphur coated urea was due to instantaneous release caused by surface cracks [23,24]. In this phase, a rate of urea release increases rapidly until it reaches a constant rate, in which, entering phase II release period.

TABLE 3. Urea release coefficients for St-Alg beads with different mathematical models and its release mechanism

#	Higuchi Model		Ritger-Peppas Model				
			0 < *t* < 7 days		t > 7 days		
	k ($days^{-0.5}$)	R^2	k ($days^{-n}$)	n	k ($days^{-n}$)	n	R^2
S1	0.1264	0.8108	0.0426	0.6625	0.0021	1.8450	0.9975
S2	0.1792	0.8624	0.3582	0.0749	0.0496	0.9020	0.9981
S3	0.2335	0.8036	0.5000	0.0600	0.1198	0.6969	0.9945
S4	0.2598	0.8069	0.5616	0.1383	0.3285	0.3657	0.9861
S5	0.1093	0.7616	0.0317	0.7724	0.0001	2.8192	0.9980
S6	0.1499	0.8639	0.2061	0.1623	0.0109	1.3492	0.9923
S7	0.1457	0.8028	0.2317	0.1502	0.0012	2.0211	0.9949
S8	0.1336	0.8334	0.2315	0.1678	0.0026	1.7359	0.9906
S9	0.1144	0.6716	0.1458	0.1474	0.0000	3.2155	0.9962
S10	0.1321	0.7773	0.2390	0.1419	0.0004	2.2795	0.9914
S11	0.1610	0.8345	0.2942	0.1561	0.0035	1.6929	0.9807
S12	0.1619	0.7596	0.3369	0.0866	0.0037	1.6817	0.9873
S13	0.1028	0.7397	0.1745	0.1237	0.0003	2.3712	0.9842
S14	0.1511	0.7473	0.2921	0.0733	0.0015	1.9573	0.9960
S15	0.1810	0.8674	0.3580	0.1108	0.1042	0.6787	0.9900
S16	0.1868	0.6776	0.4950	0.0964	0.0527	0.8477	0.9420

#	Peppas-Sahlin Model						
	0 < *t* < 7 days			t > 7 days			
	k_1 ($days^{-n}$)	k_2 ($days^{-2n}$)	n	k_1 ($days^{-n}$)	k_2 ($days^{-2n}$)	n	R^2
S1	0.0307	0.0113	0.4937	0.0051	0.0010	1.0180	0.9979
S2	0.2800	0.0874	0.0600	0.0496	0.0000	0.9020	0.9979
S3	0.4919	0.0000	0.0793	0.0000	0.1198	0.3484	0.9969
S4	0.5616	0.0000	0.1383	0.1674	0.1765	0.2198	0.9861
S5	0.0306	0.0000	0.7865	0.0001	0.0000	2.8192	0.9981
S6	0.1775	0.0278	0.1415	0.0212	0.0017	0.8740	0.9932
S7	0.1590	0.0715	0.1147	0.0053	0.0001	1.2777	0.9951
S8	0.2315	0.0145	0.1200	0.0082	0.0005	1.0576	0.9892
S9	0.1034	0.0415	0.1099	0.0000	0.0000	3.2155	0.9962
S10	0.2390	0.0000	0.1419	0.0004	0.0000	2.2795	0.9914
S11	0.2942	0.0000	0.1561	0.0035	0.0000	1.7000	0.9805
S12	0.3369	0.0000	0.0866	0.0035	0.0000	1.7000	0.9871
S13	0.1748	0.0000	0.1266	0.0003	0.0002	1.2019	0.9842
S14	0.1967	0.0950	0.0555	0.0012	0.0013	0.9976	0.9961
S15	0.2427	0.1142	0.0843	0.0937	0.0363	0.4243	0.9902
S16	0.3570	0.1540	0.0600	0.0597	0.0149	0.5367	0.9383

During phase II of the release stages (between 5 to 14 days for most samples), the urea release gained a steady state and the cumulative release maintained at constant rate. However, this steady state release was not maintained indefinitely due to the sample erosion occurred. The extremely high diffusion exponent *n* value ($n > 0.86$) during this period confirmed that a Case II release pattern occurred during the phase II and III, where swelling and sample dissolution or polymer decaying were attributed to the final release of all urea content within the period of 20 to 30 days. Samples with high alginate and lower urea content, was observed to have a slightly longer release period (5 weeks) comparing to all other samples (around 4 weeks). This was attributed to the high cross-linking matrix and hence, enhancing the polymer structural integrity against water penetration. A sample of the experimental data in the

Ritger-Peppas model for fractional urea release rate for 150 phr urea at different alginate content in the polymer matrix is shown in Fig. 3. Good agreement between the model and the actual data was obtained.

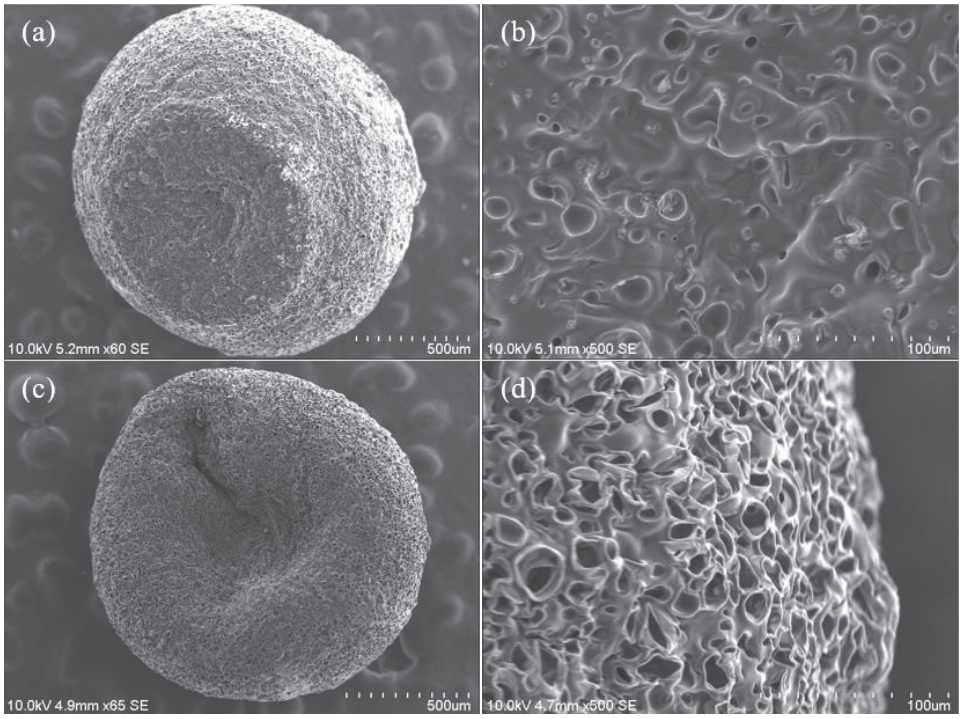

FIGURE 2. SEM images for St-Alg-U, S9 (a) fresh sample overall bead, (b) fresh sample surface morphology at 500X, (c) dried sample after 24 hour release test; (d) dried sample after 24 hours release test at 500X magnification

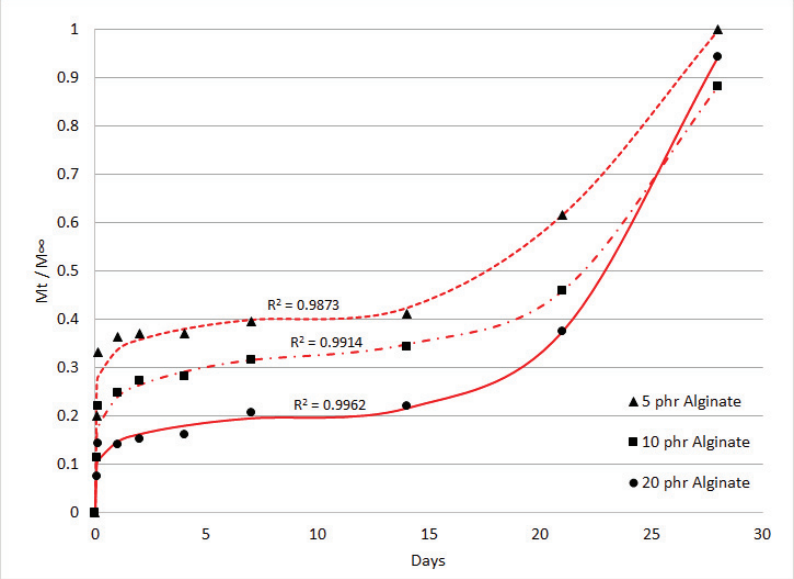

FIGURE 3. Comparison of the experimental data in Ritger-Peppas Model for cumulative urea release in water for 150 phr urea encapsulated in different alginate content.

CONCLUSION

The urea release data was fitted and compared with 3 empirical exponential equations models to support the interpretation and comprehension of the release mechanisms. The release kinetic for St-Alg CRU beads was found to have good Ritger-Peppas model fitting at R^2 value more than 0.99. The release behaviour of urea in St-Alg matrix consists of three stages: i. an extremely low diffusion exponential (n) value, indicating an initial rapid release of urea attributed to the high surface's porosity of St-Alg beads, that allowing an instantaneous water penetration into the matrix that dissolved and release the soluble content; ii. a period of linear release when the solution reaches an equilibrium while the total volume of the polymer matrix remains almost constant; and iii. an extremely high n value (>0.86) indicating the rapid "decaying release" of urea caused by the decaying of the hydrophilic polymer matrix.

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