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Utilization of Polyethylene and Paraffin Waxes as Controlled Delivery Systems for Different Fertilizers

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Paraffin and polyethylene waxes were found to be efficient as controlled delivery systems for six different commercial-grade fertilizers. These fertilizers are monoammonium phosphate, diammonium phosphate, NP, NPK-4, and NPK-14 grades, and granular triple superphosphate fertilizers. Dissolution tests were performed for matrix-type formulations in order to determine the influence of waxes on the fertilizers release rate. Three different diffusion release formulas were tested for describing the release rate of the different fertilizers. The release times were at least doubled for all of the fertilizers while using either paraffin wax or polyethylene wax. The polyethylene wax gives longer release times than the paraffin wax.

Introduction

Control release technology in agriculture includes the controlled delivery of plant nutrients such as fertilizers to a target in a manner which maximizes its use efficiency, minimizes potential negative effects associated with overdosage, and/or extends the time in which sufficient dosages are delivered.[1] The goal of controlled-release fertilizer research since the 1940s has been the development of a product that delivers its nutrients at a rate matching the demand rate of the plant to which it is applied. Such a fertilizer would represent the ultimate in use efficiency; agronomic performance, i.e., crop yield, quality, and appearance; agronomic safety; and labor savings, i.e., reduced application frequency. It also would minimize potential losses to the environment.

Numerous technologies have been developed with varying degrees of success to maximize the various benefits of controlled release.[1−5] Of these technologies, the synthetically produced controlled-release fertilizers are categorized as nitrogen reaction products, coated fertilizers, and matrix-type formulations. Nitrogen reaction products are produced by the chemical reaction of water-soluble nitrogen compounds, while the coated fertilizers achieve controlled release by coating a soluble fertilizer core (substrate) with a water-insoluble barrier which limits the access of water to the fertilizer and thus limits its dissolution rate.

Matrix-type (monolithic) formulations constitute the third major category of controlled-release systems. The active agent is dispersed in the matrix and diffuses through the matrix continuum or intergranular openings, that is, through pores or channels in the carrier phase and not through the matrix itself. The first comprehensive study on this type of fertilizers controlled release appeared in 1987 by Hepburn et al.[6] In comparison with the previously mentioned categories, matrix-type fertilizer formulations have seldom been studied. Various materials may be used to synthesize the matrix phase in which the fertilizer is dispersed. Natural or synthetics resins (rosin, asphalt, and various waxes) and natural or synthetic polymers (starch, cellulose derivatives, polyolefins, and polydiolefins and their copoly-

mers) were used in industrial practice. However, the mechanism of release from the matrix phase system is still unclear.

The first study on the application of controlled-release technology for fertilizers was initiated in 1962.[7,8] Most of the cases reported in the literature deal with reservoir-type formulations, in which a fertilizing core is encapsulated inside an inert carrier (i.e., coated fertilizers). The release of the fertilizer is controlled by diffusion through the coating. Sulfur-coated urea (SCU),[9,10] polyethylene-coated urea,[11,12] and coated superphosphate[13] provide typical examples for this class of formulations. The other method of controlling the release of fertilizer is accomplished by means of chemically controlled releasing products, such as urea−formaldehyde condensates.[14,15] Products falling into the aforementioned categories provide extremely prolonged fertilizer release.

Higuchi[16] proposed the first relationship for the release of an active agent through the pores of a slap particle, which showed that the release rate is proportional to the square root of time:

$$Q = (D(\epsilon/\tau)(2A - \epsilon C_s)C_s t)^{1/2} \qquad (1)$$

where Q is the amount of active agent released per unit area exposed, D is the diffusion coefficient of the active agent in the dissolution medium, ϵ is the porosity of the matrix, τ is the tortuosity of the matrix, A is the concentration of the active agent in the matrix, and C_s is the solubility of the active agent in the dissolution medium. Sinclair and Peppas[17] proposed the empirical equation for the release of the active agents from nonswellable devices (slabs, cylinders, and spheres):

$$Q_t = kt^n \qquad (2)$$

where Q_t is the fraction of active agent released at time t, k is a constant incorporating the characteristics of the carrier−active agent system, and n is the diffusional exponent, indicative of transport mechanisms. Schwartz et al.[19] expressed the release by the following relationship:

$$Q_t = 1 - e^{-kt} \qquad (3)$$

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Table 1. SABIC's Fertilizer Specifications

| fertilizer	specifications	fertilizer	specifications	fertilizers	specifications
MAP		DAP		NPK	
grade	11:52:0	grade	18:46:0	grade	14:38:10
ammonical nitrogen	11.0 [min]	ammonical nitrogen	18	total nitrogen wt (%)	14.0
total P_2O_5 wt (%)	52.0	total P_2O_5 wt (%)	46	ammonical nitrogen	12.0 [min]
water soluble P_2O_5 wt (%)	45.8	water-soluble P_2O_5 wt (%)	41.0 [min]	total P_2O_5 wt (%)	38.0
moisture wt (%)	1.0 [max]	moisture wt (%)	1.0 [max]	water-soluble P_2O_5 wt (%)	31.0 [min]
				total K_{20} wt (%)	10.0
				moisture wt (%)	1.0 [max]
NPK		NP		GTSP	
grade	4:29:19	grade	28:28:0	grade	0:46:0
total nitrogen wt (%)	4.0	total nitrogen wt (%)	28.0	total P_2O_5 [expected] wt (%)	47.5
ammonical nitrogen	[min]	ammonical nitrogen	9.0	available P_2O_5 wt (%)	46.0
total P_2O_5 wt (%)	29.0	total P_2O_5 wt (%)	28.0	water-soluble P_2O_5 wt (%)	43.0 [min]
water-soluble P_2O_5 wt (%)	[min]	water-soluble P_2O_5 wt (%)	25.2 [min]	free acid	4.0 [max]
total K_{20} wt (%)	19.0	moisture wt (%)	1.0 [max]	moisture wt (%)	2.0 [max]
moisture wt (%)	1.0 [max]				

where Q_t is the fraction of active agent released at time t and k is a release rate constant.

This work focuses on the study of the release characteristics of different fertilizers using paraffin and polyethylene waxes. Dissolution tests in water were conducted for this purpose. All fertilizers release kinetics obtained in this work were fitted to the Sinclair formula, modified hyperbola formula, and modified Schwartz[18] formula. These formulas describe the diffusion phenomena occurring while releasing different types of fertilizers.

Experimental Section

Materials. The fertilizers used in this work are monoamonium phosphate (MAP; grade 11:52:0), diammonium phosphate (DAP; grade 18:46:0), compound fertilizers containing either nitrogen and phosphate (i.e., NP grade 28:28:0) or nitrogen, phosphate, and potash (i.e., NPK-14 grade 14:38:10, NPK-4 grade 4:29:19), and granular triple superphosphate (GTSP; grade 0:46:0). All of these fertilizers were produced by SABIC (Saudi Arabia Basic Industries Co.). The specifications of these fertilizers are listed in Table 1. Paraffin wax with a freezing point of 57−60 °C was obtained from Winlab (U.K.), while polyethylene wax with a melting point of 106.4 °C and a viscosity of 22 cP was obtained from Advanced Engineering (U.S.).

Experimental Procedures. The preparation of the fertilizing dosage forms is mainly based on the technique illustrated in U.S. patent 5,137,563,[19] but the technique was simplified using the following procedures: Granules of SABIC fertilizers were pulverized in a hammer mill, and the fractions of 300−150 μm and less than 150 μm were collected using U.S. standard sieves. The fertilizer particles were dried in an oven dryer at 100 °C for 1 day and then kept in a desiccator over silica gel until used. An appropriate amount of either paraffin wax or polyethylene wax (i.e., 2 g) was introduced in a beaker, which in turn was placed on a hot-plate stirrer maintained at about 70−80 °C. When the wax melted, an appropriate amount of fertilizer (18 g) was gradually added to provide 90 wt % concentration of fertilizer in the matrix. The mixture was stirred during the addition of the fertilizer. Stirring was continued for some 10−15 min to ensure uniform dispersion of the fertilizer in the wax phase. After that, the melt was poured into specially designed Plexiglas molds and then was left to solidify. The fertilizing formulations were removed from the molds in the form
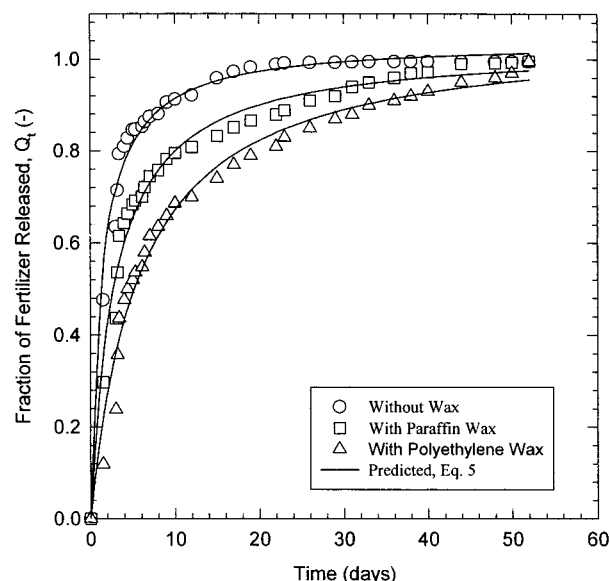
Figure 1. Release behavior of MAP fertilizer.

of small tablets (diameter 0.75 cm, height 0.35 cm, volume 0.158 mL).

The dissolution tests were carried out in deionized water in glass bottles in the absence of stirring. The glass bottles were kept at 25 ± 0.2 °C in a controlled-temperature water bath for the whole duration of the experiments. The amount of fertilizer released was assayed at various times using two different methods: electrical conductivity measurements using a conductmeter (Omega CDH-420) equipped with different electrodes and flame photometric analysis using an atomic absorption spectrophotometer (BUCK Sci. Inc. model 200A) operating in the flame mode. The results obtained by these two methods were comparable and deviated only by 0.4%. Each experiment was performed three times; thus, all of the data points illustrated in each figure represent the mean of the three experiments. The deviation of all of the data obtained was always below 2.5%.

Results and Discussion

Figure 1 shows the release behavior of MAP fertilizer. The fraction of the fertilizer released of solution was plotted versus time in days as illustrated in the figure for the fertilizer without and with wax. It is clear that the release time for the waxed MAP fertilizer released at a longer time than that of the pure MAP fertilizer.

Table 2. Summary of the Release Data for Different Fertilizers

fertilizer	total time of release without wax, days	% released fertilizer (without wax) during the first 10 days	total time of release with paraffin wax, days	total time of release with polyethylene wax, days
MAP	22	92	45	52
DAP	22	90	48	58
NP	35	91	42	48
NPK-4	23	89	45	54
NPK-14	25	96	50	64
GTSP	22	90	40	48

Table 3. Curve-Fitting Results of the Release Data for All of the Used Fertilizers

fertilizer	parameters	$Q_t = at^b$	$Q_t = at/(1 + bt)$	$Q_t = a(1 - e^{-bt})t$
MAP				
without wax	a	0.666	0.751	0.977
	b	0.117	0.721	0.397
	r^2	0.917	0.984	0.977
with paraffin wax	a	0.465	0.358	0.929
	b	0.204	0.347	0.247
	r^2	0.939	0.982	0.954
with polyethylene wax	a	0.302	0.183	0.906
	b	0.311	0.172	0.150
	r^2	0.937	0.979	0.963
DAP				
without wax	a	0.617	0.575	0.990
	b	0.134	0.543	0.324
	r^2	0.830	0.962	0.995
with paraffin wax	a	0.457	0.331	0.945
	b	0.205	0.317	0.226
	r^2	0.920	0.993	0.975
with polyethylene wax	a	0.3823	0.259	0.892
	b	0.238	0.259	0.199
	r^2	0.931	0.976	0.943
NP				
without wax	a	0.489	0.435	0.995
	b	0.215	0.394	0.285
	r^2	0.755	0.920	0.959
with paraffin wax	a	0.452	0.423	0.925
	b	0.222	0.409	0.307
	r^2	0.788	0.926	0.934
with polyethylene wax	a	0.345	0.272	0.879
	b	0.281	0.269	0.220
	r^2	0.869	0.944	0.921
NPK-4				
without wax	a	0.626	0.597	0.979
	b	0.132	0.567	0.347
	r^2	0.784	0.909	0.943
with paraffin wax	a	0.527	0.430	0.952
	b	0.173	0.412	0.279
	r^2	0.860	0.950	0.944
with polyethylene wax	a	0.339	0.204	0.933
	b	0.282	0.190	0.157
	r^2	0.922	0.978	0.962
NPK-14				
without wax	a	0.697	0.892	0.981
	b	0.0996	0.861	0.483
	r^2	0.764	0.925	0.965
with paraffin wax	a	0.472	0.362	0.941
	b	0.194	0.352	0.242
	r^2	0.902	0.987	0.967
with polyethylene wax	a	0.350	0.217	0.920
	b	0.261	0.209	0.165
	r^2	0.926	0.991	0.975
GTSP				
without wax	a	0.513	0.418	0.979
	b	0.194	0.384	0.275
	r^2	0.797	0.927	0.956
with paraffin wax	a	0.394	0.271	0.957
	b	0.261	0.248	0.199
	r^2	0.881	0.968	0.968
with polyethylene wax	a	0.287	0.174	0.937
	b	0.337	0.156	0.141
	r^2	0.926	0.984	0.979

The pure MAP fertilizer was released in 22 days while the paraffin wax treated MAP fertilizer was released during the first 45 days. The polyethylene-treated MAP fertilizer released totally during 52 days, as shown Figure 1, which is almost 2.4 times the release time of the pure fertilizer. The solid lines represent the pre-

dicted fertilizer released with time using eq 5, as will be explained in the Release Kinetics section.

Table 2 summarizes the release data for all of the fertilizers used in this work. Based on the results shown in Figure 1 and listed in Table 2, it is very clear that paraffin wax and polyethylene wax systems proved to be effective in entrapping all SABIC fertilizers, which in their conventional forms dissolve at a shorter time in water than the waxed fertilizers. Generally, the release times were at least doubled for all of the fertilizers while using either paraffin wax or polyethylene wax. The polyethylene wax gives a longer release time than the paraffin wax; however, the paraffin wax has the advantage of total degradation in the soil while the polyethylene wax turned into another pollution problem burden in the soil. The total release period of NPK-4, NPK-14, and DAP is longer than that of other fertilizers used, while the release periods of NP and GTSP fertilizers represent the shortest among all other fertilizers used.

It is important to notice that the matrix formulations technique used in this work can be used easily in industrial-scale level with a very low cost. A heating tank equipped with a pelletizer would be enough for the production of fertilizing forms. Addition of any pesticides to the fertilizer–wax matrix can be carried out during the preparation of the matrix. Because of the lower temperature used in this work, this technique does not need any type of solvent, which is necessary for any fertilizer coating technology. At the same time, the matrix formulations technique does not demand costly or complex apparatuses, such as granulation drums or fluid beds usually employed for the coating of fertilizer granules or prills.

Release Kinetics. It is very important to reveal the mechanisms governing the release of fertilizers in the dissolution medium. All of the release data for both pure and matrix formulations fertilizers were tested against the following relationships:

(1) Sinclair and Peppas formula,[17] which has the following form:

$$Q_t = at^b \qquad (4)$$

This simplified empirical formula, which was provided by Sinclair and Peppas,[17] reveals the mechanisms that govern the diffusion of any active agent through non-swellable devices (slabs, cylinders, and spheres).

(2) Modified hyperbola formula, which has the following form:[18]

$$Q_t = \frac{at}{1 + bt} \qquad (5)$$

This modified hyperbola formula was also tested in this work. The release is first order at low values of t and decreases to zero order as t increases.

(3) Modified Schwartz et al.[18] formula.

In many occasions, first-order kinetics describe the release of active agents from matrices;[18] thus, release is expressed by the following relationship:
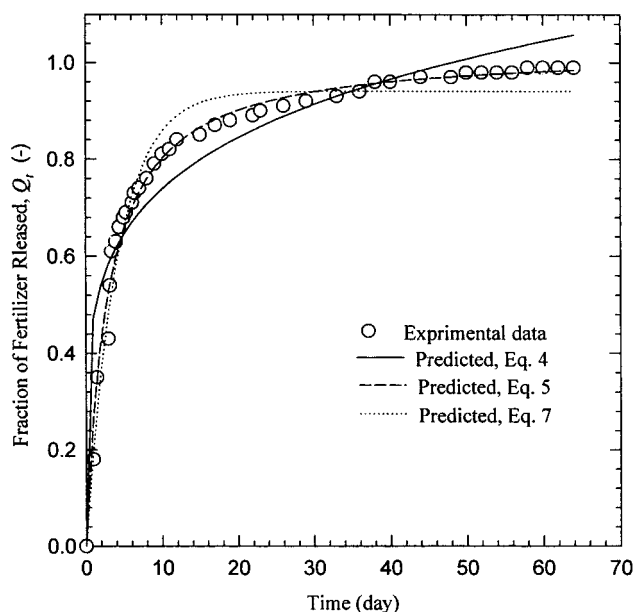
$$Q_t = 1 - e^{-bt} \qquad (6)$$

Figure 2. Comparison between the experimental data for paraffin wax treated NPK-14 fertilizer and the predicted values of the fraction fertilizer released calculated by eqs 4, 5, and 7.

Therefore, we modified Shwartz formula to have the following form:

$$Q_t = a(1 - e^{-bt}) \qquad (7)$$

In all of these equations (4–7), Q_t is the fraction of fertilizer released at a time t, while a and b are the release constants.

The fitting results of these three release formulas are listed in Table 3. As is clearly shown in Table 3, both eqs 5 and 7 fit the release data better than eq 4. Figure 2 shows a comparison between the experimental data for paraffin wax treated NPK-14 fertilizer and the predicted values of the fraction fertilizer released calculated by eqs 4, 5, and 7. As is clearly shown in the figure, eq 5 represents the best fit for the experimental data of paraffin wax treated NPK-14 fertilizer. The fraction of fertilizer released predicted by eqs 5 and 7 approaches 1 as time increases, whereas the fraction predicted by eq 4 cannot approach 1 as time increases, as is illustrated in Figure 2. For MAP and DAP fertilizers, eq 5 represents the best fit among the three formulas for describing the release data, as is clearly reflected through the value of r^2 (correlation coefficient). For NP, NPK-4, NPK-14, and GTSP fertilizers, eq 5 followed by eq 7 fits the release data better than eq 4.

Conclusions

The paraffin and polyethylene wax systems proved to be effective in entrapping MAP, DAP, NP, NPK-4, NPK-14, and GTSP fertilizers, which in their normal forms (i.e., without wax treatment) dissolve in water in a shorter time than the wax-treated fertilizers. The method of preparation of the wax–fertilizer matrix used in this work does not need a complicated and costly setup or any solvent, which makes this technique quite competitive and with a low-energy demand. In this work, the amount of the fertilizer released from the matrix in a given time was affected by the type of wax used. The released times were at least doubled for all of the fertilizers while using either paraffin wax or

polyethylene wax. The polyethylene wax gives a longer release time than the paraffin wax; however, the paraffin wax has the advantage of total degradation in the soil. The modified hyperbola formula gives the best fit for describing the release data of different fertilizers used in this work.

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