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*Review Article*

# Meticulous Overview on the Controlled Release Fertilizers

**Siafu Ibahati Sempeho,[1] Hee Taik Kim,[2] Egid Mubofu,[3] and Askwar Hilonga[1]**

[1] *Department of Materials Science and Engineering, Nelson Mandela African Institution of Science and Technology, P.O. Box 447, Arusha, Tanzania*
[2] *Department of Chemical Engineering, Hanyang University, 1271 Sa 3-dong, Sangnok-gu, Ansan-si, Gyeonggi-do 426-791, Republic of Korea*
[3] *Chemistry Department, University of Dar es Salaam, P.O. Box 35091, Dar es Salaam, Tanzania*

Correspondence should be addressed to Askwar Hilonga; askwar.hilonga@nm-aist.ac.tz

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Owing to the high demand for fertilizer formulations that will exhaust the possibilities of nutrient use efficiency (NUE), regulate fertilizer consumption, and lessen agrophysicochemical properties and environmental adverse effects instigated by conventional nutrient supply to crops, this review recapitulates controlled release fertilizers (CRFs) as a cutting-edge and safe way to supply crops' nutrients over the conventional ways. Essentially, CRFs entail fertilizer particles intercalated within excipients aiming at reducing the frequency of fertilizer application thereby abating potential adverse effects linked with conventional fertilizer use. Application of nanotechnology and materials engineering in agriculture particularly in the design of CRFs, the distinctions and classification of CRFs, and the economical, agronomical, and environmental aspects of CRFs has been revised putting into account the development and synthesis of CRFs, laboratory CRFs syntheses and testing, and both linear and sigmoid release features of CRF formulations. Methodical account on the mechanism of nutrient release centring on the empirical and mechanistic approaches of predicting nutrient release is given in view of selected mathematical models. Compositions and laboratory preparations of CRFs basing on *in situ* and graft polymerization are provided alongside the physical methods used in CRFs encapsulation, with an emphasis on the natural polymers, modified clays, and superabsorbent nanocomposite excipients.

## 1. Introduction

Controlled release fertilizers (CRFs) are fertilizer granules intercalated within carrier molecules commonly known as excipients to control nutrients release thereby improving nutrient supply to crops and minimize environmental, ecological, and health hazards [1]. In that sense, CRFs usage is an advanced way to supply crop's nutrients (cf. conventional ways) due to gradual pattern of nutrient release, which improves fertilizer use efficiency (FUE) [2]. In other words, depending on the thickness of the coatings within the formulation, CRFs enable nutrients to be released over an extended period leading to an increased control over the rate and pattern of release [3], consequently the excipients play a role in regulating nutrients release time and eliminate the need for constant fertilization and higher efficiency rate than conventional soluble fertilizers [1].

Occasionally the terms controlled release fertilizers (CRFs) and slow release fertilizers (SRFs) have been used interchangeably, yet they are different. Typically, the endorsed differences between slow-release and controlled-release fertilizers are not clear [4, 5]. However, the term CRF is generally applied to fertilizers in which the factors dominating the rate, pattern, and duration of release are well known and controllable during CRF preparation [5, 6]. SRFs on the other hand are characterized by the release of the nutrients at a slower rate than is usual but the rate, pattern, and duration of release are not well controlled [5, 6]; they may be strongly affected by handling conditions such as storage, transportation, and distribution in the field, or by soil conditions such as moisture content, wetting and drying, thawing and freezing, and biological activity [7–9]. Thus, while in SRFs the nutrient release pattern is fully dependent on soil and climatic conditions and it cannot be predicted (or *only* very roughly)

[10]; with CRFs, the release pattern, quantity, and time can be predicted within certain limits. For example, the classification of sulphur-coated urea (SCU) is subject to debate [5] due to a significant variation in the release patterns between different batches of fertilizer [5, 6, 11]. As a result, SCU is considered to be SRF despite being debated.

CRFs use is associated with several economic, agronomical, and environmental returns. Economically, CRFs supply nutrients to the crops for the entire season through a single application thereby saving spreading costs and reduce the demand for short-season manual labour required for topdressing operations [7]. Agronomically, CRFs usage is associated with the improvement of plant growth conditions, such as reduction of stress and specific toxicity resulting from excessive nutrient supply in the root zones. Similarly, CRFs increase the availability of nutrients due to the controlled release of nutrients into a "fixing" medium during the fixation processes in the soil as well as supplying nutrients in the forms preferred by plants; in that way the synergistic effect between nutrients in the CRFs is enhanced [7]. From the environmental perspective, CRFs improves NUE and in so doing reduces losses of surplus nutrients (over plant needs) to the environment [7]. Consequently, high levels of fertilizer accumulation in the environment are minimized, thereby lessening several environmental problems associated with conventional fertilizer use such as eutrophication which causes $O_2$ depletion, death of fish, unpleasant odour to the environment, and aesthetic problems [7, 12, 13].

## 2. Classification of CRFs

Several classifications of CRFs have been proposed. In this review, we will attempt to discuss a few of them. Based on Shaviv's grouping [6], CRFs may be classified as follows.

*2.1. Organic-N-Low-Solubility Compounds.* These can be subdivided into biologically decomposing compounds usually based on urea-aldehyde condensation products, such as urea-formaldehyde (UF), urea-triazone (UT), crotonylidene diurea (CDU), and chemically decomposing compounds, such as isobutylidene-diurea (IBDU). Succinctly, UF is prepared by reacting excess urea under controlled conditions of pH, temperature, U-F ratio, and reaction time. UT solution is based on the reaction of urea-ammonia-formaldehyde. CDU is prepared by reacting urea with acetaldehyde under the catalysis of an acid. IBDU is prepared by reacting liquid isobutyraldehyde with solid urea [5, 7, 10, 14].

*2.2. Fertilizers in Which a Physical Barrier Controls the Release.* These can be subdivided into granules coated by hydrophobic polymers or as matrices in which the soluble active material is dispersed in a continuum that restricts the dissolution of the fertilizer. The coated fertilizers can further be divided into fertilizers with organic polymer coatings that are either thermoplastic or resins and fertilizers coated with inorganic materials such as sulphur or mineral based coatings. The materials used for preparation of matrices can also be subdivided into hydrophobic materials such as polyolefins and rubber and gel-forming polymers (hydrogels) which are hydrophilic in nature. Broadly, the use of coated fertilizers in agricultural practices is quite common as compared to the use of matrices. For instance, sulphur-coated urea (SCU) was developed at the Tennessee Valley Authority laboratories and manufactured commercially for almost 30 years [7, 15]. Its preparation is based on coating preheated urea granules with molten sulphur. The CRF alkyd-type resin-coated fertilizer (Osmocote) was first produced commercially in California in 1967. It is a copolymer of dicyclopentadiene with a glycerol ester [7]. In fact, these formulations control the rate of nutrient release offering multiple environmental, economic, and yield benefits [16]. Gel-based matrices are still being developed [17].

*2.3. Inorganic Low-Solubility Compounds.* This type of CRFs includes fertilizers such as metal ammonium phosphates (e.g., $MgNH_4PO_4$) and partially acidulated phosphate rocks (PAPR). Besides, the biologically and microbially decomposed N products, such as UF, are commonly referred to in the trade as slow-release fertilizers and coated or encapsulated/occluded products as controlled-release fertilizers [5, 7]. Essentially, Zhang et al.'s writings provide a deep detailed account on the subject in a much more broad sense [18].

## 3. Preparation of CRFs Formulations

Slowing the release of plant nutrients from fertilizers can be achieved by different methods and the resulting products are known as slow- or controlled-release fertilizers. With controlled-release fertilizers, the principal method is to cover a conventional soluble fertilizer with a protective coating (encapsulation) of a water-insoluble, semipermeable or impermeable-with-pores material. This controls water penetration and thus the rate of dissolution and ideally synchronizes nutrient release with the plants' needs. The most important manufactured materials include (i) materials releasing nutrients through either microbial decomposition of low solubility compounds, for example, organic-*N* low-solubility compounds, such as urea-aldehyde condensation products, or chemically decomposable compounds, for example, IBDU [5, 6]; (ii) materials releasing nutrients through a physical barrier, for example, sulphur-coated urea (SCU) [5]; (iii) materials releasing nutrients incorporated into a matrix, which itself may be coated, including gel-based matrices, which are still under development [5, 6, 17]; materials releasing nutrients in delayed form due to a small surface-to-volume ratio, for example, super-granules, briquettes, tablets, spikes, plant food sticks [5], and others [19–21].

According to Liu et al. [22], intercalation of nutrients into the excipients is normally achieved by two methods. In the first method, the compound to be loaded is added to the reaction mixture and polymerized *in situ* whereby the compound is entrapped within the gel matrix, whereas in the second method, the dry gel is allowed to swell in the compound solution and after equilibrium swelling, the gel is dried and the device is obtained. This involves

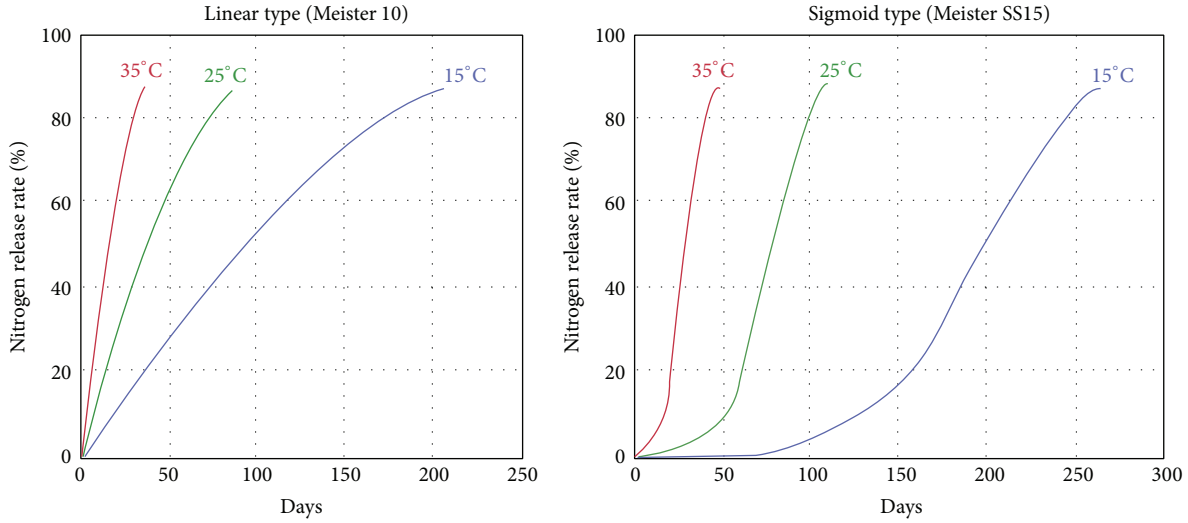



Figure 1: The effect of temperature on the release rate of Meister.

graft-polymerization [23–26]. The benefits and drawbacks are that for the former method, the entrapped compound may influence the polymerization process and the polymer network structure; while for the latter, the loaded compound always accumulates on the surface during the drying of the loaded hydrogel, which consequently leads to a "burst effect"; moreover, the loading amount may be low if the compound affects the water absorbency strongly.

Typical physical methods for encapsulating fertilizers include spray coating, spray drying, pan coating, and rotary disk atomization. Special equipment for these methods are rotary drum, pan or ribbon or paddle mixer, and fluidized bed [1]. The details of these methods are beyond the scope of this paper.

## 4. Nutrient Release in the CRFs Context

In this perspective, with regard to the European Standardization Committee (CEN), nutrient release (of course from the excipients) can be manifest by the transformation of a chemical substance or rather fertilizer nutrients into a plant-available form (e.g., dissolution, hydrolysis, degradation, etc.), whereas slow release is the release wherein the rate of a nutrient release from the fertilizer is slower than that from a fertilizer in which the nutrient is readily available for plant uptake [27]. CEN's declaration alleged that "fertilizer should be described as CRFs if at room temperature the nutrients released exceed 15% in 24 hours, or no more than 75% released in 28 days, or at least about 75% released at the stated release time" [5, 7] giving different release patterns. That is to say, CRFs that do not meet these three CEN's criteria are nonpertinent for the subject of controlled release formulations since the patterns will not comply with the standard ones, namely, linear and sigmoidal release patterns (Figure 1).

As mentioned above, release patterns can be classified into linear and sigmoidal release types [5, 28]. Examples

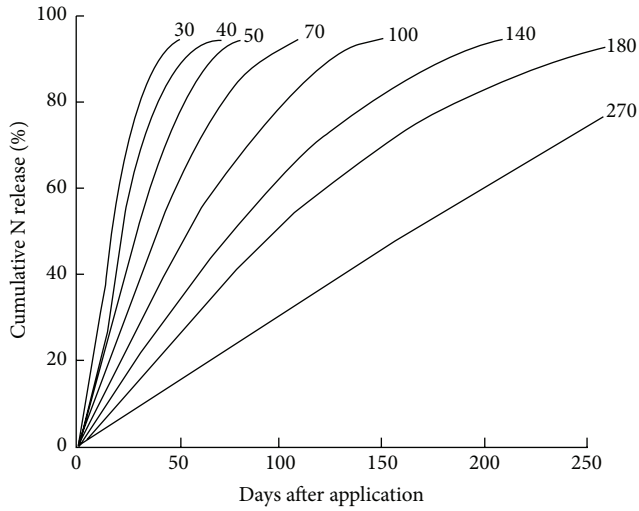



Figure 2: Linear release pattern.

of linear-release formulations presenting nutrient release between 30 and 270 days at 25°C for Meister formulation are given in Figure 2, whereas for sigmoidal-release formulations presenting nutrient release between 40 and 200 days at 25°C for Meister are shown in Figure 3 [5].

Actually, the characteristic features of CRFs encompass the release pattern (i.e., shape, lag, lock off); release duration; differential release between N, P, and K; effect of temperature on release; effect of the medium/environmental conditions on release [5, 6]. In most cases, the energy of activation of the release, $EA_{rel}$, is calculated on the basis of estimates of the rate of the release (% released per day) during the linear period obtained from the release curves [14].

As far as CEN's definition of release is concerned, the example from Meister formulation described above should comply with the criterion that at least about 75% of nitrogen should be released at the stated release time for this CRF to

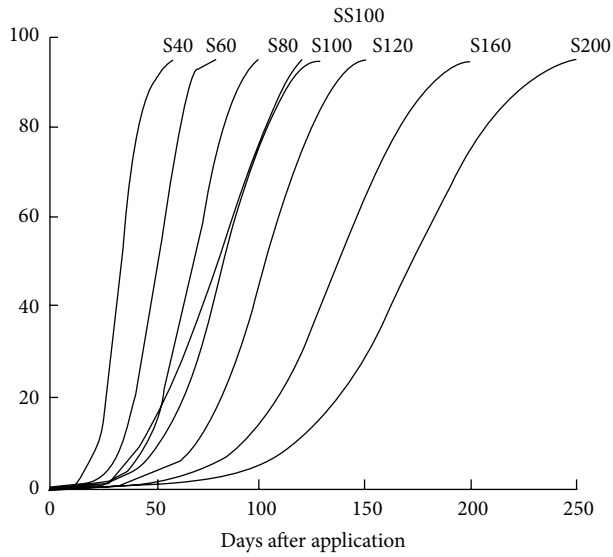



FIGURE 3: Sigmoidal release pattern.

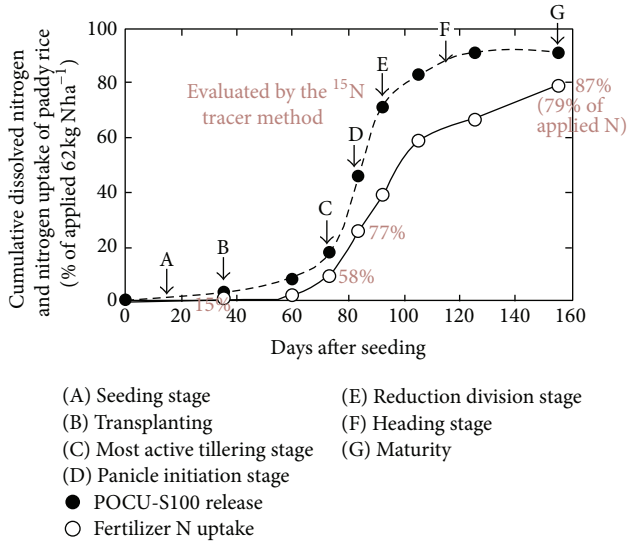



FIGURE 4: Relationship between dissolved N and fertilizer derived N uptake of paddy rice.

be approved. As a matter of fact, Kanno [29] indicated that at the end of 160 days the nitrogen intake reached 79% of the applied N (Figure 4) and so conforming to CEN's conditions.

In point of fact, establishing nutrient release profiles requires data from both field testing and laboratory testing. In the laboratory, release of nutrients from the excipients is done using water and soil matrices [5, 30]. Field testing involves net bags placed in the ploughed layer of soil in the actual field [5, 30]. Industrial methods involve extract at 25°C, 40°C, and 100°C [5]. However, Du et al. [14] provide a new procedure where release characteristics are tested in three different systems, namely, (i) free water (which he termed common procedure); (ii) water saturated sand packed in columns; (iii) sand at field capacity moisture.

## 5. Mechanism of Nutrients Release from CRFs Formulations

Consistent experimental data with reference to release phenomena of nutrients from polymer coated CRFs are indispensably beneficial for better agronomic and environmental results [14]. Agric [31], after a period of laboratory testing of Meister CRFs, obtained the results described in Tables 1 and 2 for both linear and sigmoid patterns. The designed formulation which is marketed as Meister has its mechanism proposed by the company and the summary is given in Figure 5. The mechanism is based on three significant steps, namely, water adsorption, dissolution of urea, and leaching.

In addition to that, Guo et al. [32] proposed the mechanism of nitrogen release from urea-formaldehyde (UF) slow-release fertilizer granules based on three steps. *Step one:* the coating materials become swollen by absorbing water from the soil and so get transformed into hydrogels which contribute to increasing the orifice size of the 3D network of the coating materials so that it benefits the diffusion of the fertilizer in the core of the gel network. As a result, a layer of water between the swollen coatings and the UF granule core is formed. *Step two:* water slowly diffuses into the cross linked polymer network and dissolves the soluble part of UF; consequently the soluble part of the fertilizer gets slowly released into the soil through the swollen network with the dynamic exchange of the water in the hydrogel and the water in the soil. *Step three:* the soil microorganisms penetrate through the swollen coatings and assemble around the UF granule thereby degrading the insoluble part of nitrogen in UF granule into urea and ammonia which in turn is slowly released into the soil via dynamic exchange. Such steps have also been described as lag period, linear stage, and decay period by other researchers [14].

This mechanism can be adapted to effectively explain the release behaviour in other CRF formulations. Different mathematical mechanistic models based on empirical and mechanistic approaches plus empirical and semiempirical models have been proposed for prediction of the nutrient release using chemophysical parameters as will be discussed in the coming sections. Nevertheless, most mechanisms reveal that nutrients release from CRFs is mainly controlled by diffusion mechanism with respect to temperature, thickness of the coating material, type of nutrient, and the presence or absence of the relevant soil microorganisms.

## 6. Predicting Nutrient Release from CRFs

Profoundly, a number of empirical and semiempirical mechanistic mathematical models have been put forward in order to provide realistic theoretical assumptions connected to the patterns of nutrients release mechanisms based on the nature and the properties of the delivery systems (DS) [7], and in that case, release models have been used as tools for improving the CRFs' design methodology leaving behind conceivable breakthroughs in assessing prospective hazards such as leaching or volatilization losses and effects such as "bursting" or "tailing effect" [7–9]. Such conceptual approaches include the diffusion model, zero order

Table 1: Linear release pattern.

| Brand name | 80% release (days at 20°C) | 80% release (days at 25°C) | Japanese brand name | N content (%) |
|---|---|---|---|---|
| MEISTER-5 | 50 | 30 | LP-30 | 42 |
| MEISTER-7 | 70 | 40 | LP-40 | 42 |
| MEISTER-8 | 80 | 50 | LP-40 | 50 |
| MEISTER-10 | 100 | 70 | LP-70 | 42 |
| MEISTER-15 | 150 | 100 | LP-100 | 42 |
| MEISTER-20 | 200 | 140 | LP-140 | 42 |
| MEISTER-27 | 270 | 180 | LP-180 | 42 |
| MEISTER-40 | 400 | 270 | LP-270 | 42 |

Table 2: Sigmoid release pattern.

| Brand name | Time lag days/release days | | Japanese brand name | N content (%) |
|---|---|---|---|---|
| | at 20°C in soil | at 25°C in soil | | |
| MEISTER-5 | 35/35 | 20/20 | LP-S40 | 41 |
| MEISTER-7 | 45/45 | 30/30 | LP-S60 | 41 |
| MEISTER-8 | 60/60 | 40/40 | LP-S80 | 41 |
| MEISTER-10 | 45/105 | 30/70 | LP-S100 | 41 |
| MEISTER-15 | 70/80 | 45/55 | LP-SS100 | 41 |
| MEISTER-20 | 90/90 | 60/60 | LP-S120 | 41 |
| MEISTER-27 | 120/120 | 80/80 | LP-S160 | 41 |
| MEISTER-40 | 150/150 | 100/100 | LP-S200 | 41 |

kinetics model, first order kinetics model, Higuchi model, Korsmeyer-Peppas model, Hixson-Crowell model, Weibull model, Baker-Lonsdale model, Hoffenberg model, sequential layer model, Couarraze model, and Peppas-Sahlin model. In particular, most of the proposed release models assume that the release of nutrients from coated CRFs is either controlled by the rate of solute diffusion from the fertilizers or by the rate of water/vapour penetration into the CRF through the coating [7].

*6.1. Diffusion Model.* Considering a mathematical model developed for urea release from sulphur-coated granules under soil conditions [7, 33], the assumption was that urea diffuses from the granule through pores or holes caused by erosion of the coating and that the transport is influenced by temperature and soil water content; thus, diffusion occurs through the coating. This model was verified using Fick's first law as

$$\frac{dm}{dt} = -DS_k \frac{dC_k}{dx_k}, \tag{1}$$

where $m$ is the mass of urea diffusing out of the granule, $D$ is the effective diffusion coefficient of urea in water, $S_k$ is the cross-sectional area through which diffusion occurs, and $C_k$ is the urea concentration. The subscript $k$ is the value for the internal pore coating or outside segments [7]. The predictive power of this model is certainly restricted to the fact that particle flux is directly proportional to the spatial concentration gradient. Nonetheless, it is not the spatial concentration gradient that causes particle movement, that is, particles do not push each other [34]. That is to say, particles do exhibit random motion on the molecular level and this random motion ensures that a tracer will diffuse thereby decreasing the concentration gradient [34].

Moreover, a study by Jarrell and Boersma [35] revealed that the diffusion of urea through the sulphur coating occurred in two steps represented in the following models:

$$\begin{aligned} \frac{dm_r}{dt} &= \frac{DS_p}{M_o l} C_{\text{sat}} \quad \text{for } t < t_1, \\ \frac{dm_r}{dt} &= \frac{DS_p}{M_o l} (1 - m_r)\, \rho, \quad \text{for } t > t_1, \end{aligned} \tag{2}$$

where $m_r = m/M_o$, while $M_o$ is the initial mass of urea in the granule, $C_{\text{sat}}$ is the concentration of saturated urea solution, $l$ is the coating thickness, $\rho$ is the density of solid urea, and $t_1$ is the onset of the period of the decaying rate of release as the solution inside the granule becomes unsaturated.

Similarly, this study is also boundless for the reason that it ignores some important factors and features that are relevant to diffusion of active bioactive substances from an excipient or rather a membrane-coated granule (sphere). It is for that reason that the following Arrhenius type of model pertaining to the diffusion coefficient $D$ was suggested [7, 33, 36]:

$$D = ATe^{(-\text{EA}_{\text{realese}}/T)}, \tag{3}$$

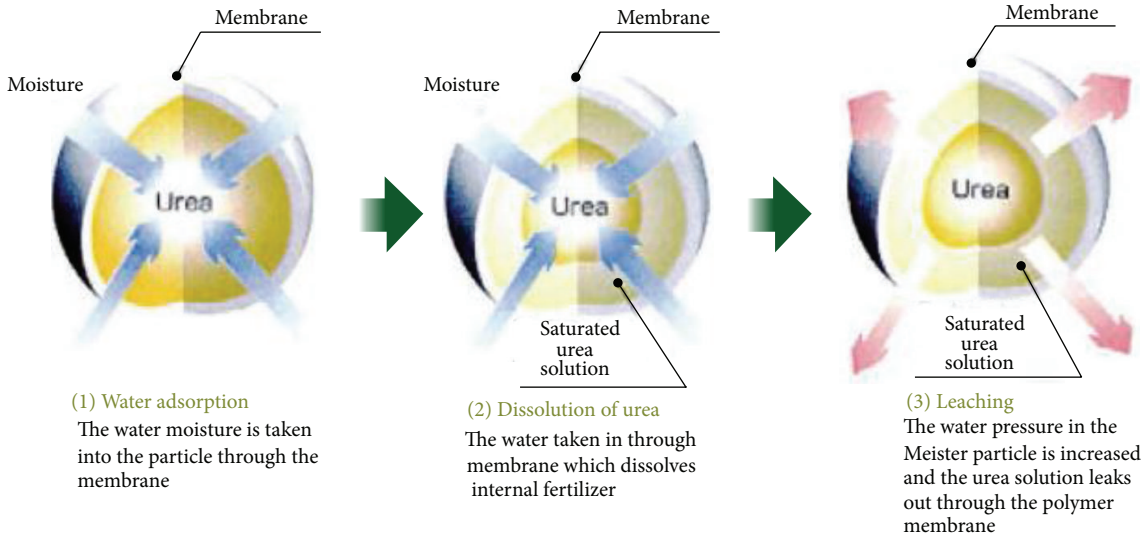



Figure 5: Release of nitrogen from polyolefin coated urea in water at 25°C.

where $T$ is the kelvin absolute temperature and $EA_{release}$ stands for the apparent energy of activation for urea diffusion from the excipients. This expression as proposed provides a conceivable explanation for the temperature dependence on the CRFs release rates. On the same side, a similar model for simulating nutrients release from the CRFs in a 1D coordinate system is known [37]; however, an additional assumption in favour of this model is that the diffusion coefficient is time dependent, thus giving the following expression:

$$D = D_0 t^n, \tag{4}$$

where $t$ is time, $D_0$ is an initial value at $t = 0$, and $n$ is an empirical constant. The time dependence of $D$ presents a lag in the curve describing cumulative release with time (i.e., sigmoidal release pattern) which could otherwise not have been obtained by simply applying Fick's law described before [7].

*6.2. Sequential Layer Model.* This model assumes that during the release of an active ingredient from the hydrophilic excipients, significant water concentration gradients are formed in the first place at the matrix/water interface and by so doing there is a creation of water imbibition into the system and as a result, and there occur dramatic physicochemical changes, namely, the exact geometry of the active substance within the excipients, axial and radial direction of the mass transport, and water diffusion coefficient on the matrix. Due to swelling of the excipients following water imbibition phenomenon, the concentration of participating species (i.e., polymer and a chemical substance) significantly changes thereby causing increased dimensions of the system. Consequently, the dissolution of the active ingredient occurs and so it diffuses out of such hydrophilic system following concentration gradients. Essentially, the amount of water available for dissolution is directly proportional to the diffusion coefficient of the active substance within the excipients. In that view, dissolution rate constant, $k_{diss}$, of the active ingredient-excipient system can be computed and is given as

$$M_{pt} = M_{po} - k_{diss} A_t t, \tag{5}$$

where $M_{pt}$ and $M_{po}$ are the dry polymer matrix mass at time $t$ and $t = 0$, respectively; $A_t$ is the surface area of the device at time $t$ [20, 38–45].

*6.3. Hopfenberg Model.* The primary assumption in this model is that nutrients are released from the surface-eroding excipients possessing some geometries ranging from slabs, spheres, and infinite cylinders displaying heterogeneous erosion. This approach can be mathematically expressed as

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{k_o t}{C_o a}\right)^n, \tag{6}$$

where $M_t$ is the concentration of the chemical substance dissolved in time $t$, $M_\infty$ is the total matrix (chemical-excipient) concentration dissolved when the system is exhausted, $k_o$ is the erosion rate constant, $C_o$ is the initial concentration of chemical substance/fertilizer in the matrix, and $a_o$ is the initial radius for a sphere of cylinder or the half-thickness for a slab. The value of $n$ is 1, 2, and 3 for a slab, cylinder, and sphere, respectively [20, 38–45].

*6.4. Weibull Model.* As far as CRFs formulation is concerned, this model accounts for the release of nutrient molecules from the erodible matrix formulations with an assumption that factors influencing the overall release rate are exclusively mass dependent, while other factors stand to be time dependent [38]. The model depicts that a plot of logarithm of the amount of nutrient molecules dissolved in an excipient' solution versus the logarithm of time will be linear and it is mathematically given as

$$\text{Log}\left[-\ln\left(1 - m\right)\right] = b \log\left(t - T_t\right) - \log a, \tag{7}$$

where $a$ relates to the time scale of the process corresponding to the ordinate $[-\ln(1-m)] = 1$. $T_t$ refers to the lag time before the onset of the release process, $t$ is time after release phenomena, $b$ is the shape parameter corresponding to the ordinate value $(1/a)$ when time $t = 1$, and $m$ relates to the fraction of the active ingredient in the excipient' solution at time $t$ [20, 38–45].

Despite limitations associated with this model including the inability to sufficiently characterize the release kinetics of the nutrient molecules and the limited use for establishing *in vivo*/*in vitro* correlation, the model is known to be grander in the fact that the release half-life can easily be calculated and also the errors associated with it are only single figures, that is, minimum. In fact, the number of single figure errors is known to be higher than other models [38].

*6.5. Korsmeyer-Peppas Model.* Based on the CRFs context, this semiempirical model is effective in the determination of the concentration of nutrient molecules released from the excipients' membranes. Theoretically, the simple expression allied to this model is given as

$$f_t = at^n, \tag{8}$$

where $a$ refers to a constant incorporating structural and geometric characteristics of the given active substance, $n$ is the release exponent indicative of the release mechanism, and $t$ is fractional release of active substance $[M_t/M_\infty]$ described in (6) above [40].

*6.6. Higuchi Model.* Predominantly, this model explicates the release of water soluble and low soluble nutrient substances merged into the semisolid or solid excipients molecules; it has been lengthily applied in the diffusion matrix formulations. The assumption core to this model stipulates that initial concentration of the nutrient molecules incorporated into the matrix is much higher than the solubility of the former [41]. Another assumption states that the diffusion of the nutrient molecules with excipients takes place only in one dimension such that the edge effect is negligible. The third one depicts that nutrient particles are much smaller than the system thickness. Also, matrix swelling and dissolution are negligible and so diffusivity of an active nutrient substance is constant; the last assumption is that perfect sink conditions are always attained in the release environment [41].

Considerably, the assumptions underlying this model reveal that there are two systems which may be considered when formulating mathematical expression for the release systems. Such systems are as follows: (i) when the nutrient molecules are dispersed in a homogeneous uniform matrix, which of course acts as diffusional mechanism and (ii) when they are incorporated into the planar heterogeneous matrix where their concentration in the matrix is lower than their solubility such that release process occurs through pores in the excipients by penetrative leaching out [44]. Conceptually, Figure 6 can be used to formulate a language to express this model.

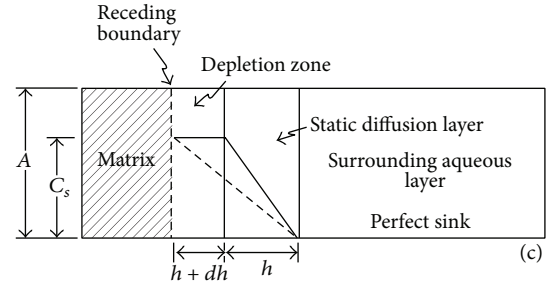



Figure 6: Conceptual Higuchi model.

According to Fick's first law,

$$\frac{dM}{Sdt} = \frac{dQ}{dt} = \frac{DC_s}{h}. \tag{9}$$

At this instant, when the nutrients molecules are dispersed within the homogeneous excipient matrix, the borderline indicated by the dashed vertical line (Figure 6) moves to the left by an infinitesimal distance ($dh$) and the infinitesimal amount ($dQ$) of the nutrients released because of this shift is given as

$$dQ = Adh - \frac{1}{2}C_s dh. \tag{10}$$

When (10) is substituted in (9), (11) is obtained and is given as

$$\frac{DC_s}{h} = \left(A - \frac{1}{2}C_s\right)\frac{dh}{dt}. \tag{11}$$

Basied on Narender's derivation steps [44], it is possible to follow Higuchi's steps for derivation as follows:

$$\begin{aligned} 2A - \frac{C_s}{2DC_s}\int h dh &= \int dt, \\ t &= \left(2A - C_s\right)\frac{h^2}{4DC_s} + C. \end{aligned} \tag{12}$$

Integrating "C" when $h = 0$, (13) is obtained as

$$h = \left(\frac{4DC_s t}{2A - C_s}\right)^{1/2}. \tag{13}$$

Recall (10) as follows:

$$dQ = Adh - \frac{1}{2}C_s dh. \tag{14}$$

This equation can be integrated to take the following simple form:

$$Q = hA - \frac{1}{2}hC_s. \tag{15}$$

Substituting (15) into (14), we obtain the Higuchi equation for the homogeneous nutrient-excipients matrices as follows:

$$Q = \left[D\left(2A - C_s\right)C_s t\right]^{1/2}. \tag{16}$$

This can be further simplified to take a form of

$$f_t = Q = A\sqrt{D\left(2C - C_s\right)C_s t}, \tag{17}$$

where $Q$ is the concentration of the given nutrient released in time $t$ per unit area $A$, $C$ is the initial concentration of the nutrient, $C_s$ is the nutrient solubility in the matrix media, and $D$ is the diffusivity of the nutrients molecules (diffusion coefficient) in the matrix substance [41, 44].

On the other hand, the heterogeneous nutrient-excipient matrix system takes a different form and in that way (16) is modified in order to take into account the porosity and tortuosity of the matrix. Conceptually, the mathematical expression will be

$$\frac{dQ}{dt} = \left(\frac{ADC_s}{2t}\right)^{1/2}, \tag{18}$$

where $dQ/dt$ is the concentration of nutrients released at time $t$, $A$ is the total amount of nutrients in unit volume of matrix, $D$ is the diffusion coefficient of the nutrients in matrix, $C_s$ is the solubility of the nutrients in polymeric matrix, and $t$ is the time [41, 44].

*6.7. Hixson Crowell Model.* This model assumes that the release rate of a nutrient molecules contained in a polymeric excipient is limited to the dissolution rate of its particles and not by the diffusion that could take place through polymeric matrix. The assumptions underlying this model include the following: (i) dissolution occurs normally to the surface of the solute particles, (ii) agitation is uniform all over the exposed surfaces and there is no stagnation, and also (iii) the particle of solute retains its geometric shape [20, 38–45].

According to Narender [44], the radius of a given bioactive particle is given as $r$ and surface area is thus $4\pi r^2$. For that reason, during release process the radius is reduced by $dr$ and so the infinitesimal volume of one particle fragment lost can be differentiated to be

$$dV = 4\pi r^2 dr. \tag{19}$$

However, infinitesimal volume of $n$ particle fragment lost can be differentiated as

$$dV = 4N\pi r^2 dr. \tag{20}$$

Recalling (20), the surface of $n$ particles can be found as

$$S = 4N\pi r^2. \tag{21}$$

From the Noyes-Whitney law, the infinitesimal change in weight is given by the equation

$$dW = kSC_s dt. \tag{22}$$

Then, the density of the nutrient molecules in the matrix could be multiplied by the infinitesimal volume change as $\rho dV = dW$ to give the following equation:

$$\rho dV = kSC_s dt. \tag{23}$$

Substituting (20) into (21) and (23), (24) is obtained as

$$-4\rho N\pi r^2 dr = 4N\pi r^2 KC_s dt. \tag{24}$$

Equation (24) can be simplified further by integrating it with respect to $r = ro$, at $t = 0$ to give the following expression:

$$r = ro - \frac{kC_s t}{\rho}. \tag{25}$$

Equally, it is possible to substitute the radius in (25) with the weight of $n$ particles to give the following expression:

$$W^{1/3} = \left(\sqrt[3]{N\rho\frac{\pi}{6}}\right)d. \tag{26}$$

Since the diameter $d$ can be substituted for $2r$, then it is possible to substitute $d$ from (25) with $2r$ from (26) to yield the Hixson-Crowell cube root equation as follows:

$$W_o^{1/3} - W_t^{1/3} = \kappa t, \tag{27}$$

where $W_o$ is the initial concentration of nutrient molecules in the matrix, $W_t$ is the remaining concentration of nutrient molecules in the matrix at time $t$, and $\kappa$ (kappa) is a constant incorporating the surface-volume relation [44].

*6.8. Zero Order Kinetics Model.* This model describes the delivery system at which the concentration of nutrients released per unit time is constant. This model assumes that in the course of dissolution process the area does not change and no equilibrium conditions are obtained. In that case, this model has been useful in the release of bioactive species/nutrients from the matrix that do not disaggregate and release the nutrients slowly from the excipients. Mathematically, the model can be expressed as

$$Q_o - Q_t = K_o t, \tag{28}$$

where $Q_t$ is the amount of nutrients dissolved in time $t$, $Q_o$ is the initial amount of nutrients in the solution (most times, $Q_o = 0$), and $K_o$ is the zero order release constant expressed in units of concentration/time. According to Mahat [42], the zero order release kinetics account for various different mass transport phenomena such as diffusion of water and bioactive species and the swelling and degradation of the excipients.

*6.9. First Order Kinetic Model.* This model is applied in the release kinetics to describe the absorption and elimination of the bioactive ingredients/nutrients from the excipients. This model assumes that a graph of release data versus time will be linear. Conferring to this model, the rate of bioactive species released from the excipients matrix is directly proportional to the concentration; that is to say, the release rate of nutrient molecules is concentration dependent [39]. Mathematical expression for this model is given as

$$\ln Q_t = \ln Q_0 + k_t, \tag{29}$$

where $Q_t$ is the concentration of nutrients yet to be released at time $t$, $Q_0$ is the concentration of nutrients yet to be released at time zero, and $k_t$ is the first order release constant.

*6.10. Baker-Lonsdale Model.* This model was established from the Higuchi model in an attempt to describe the dissolution of bioactive species from spherical matrix based excipients and hence it has been quite suitable model for microcapsules or microspheres systems. In a very simplified form it is possible to express this model as

$$F_t = \frac{3}{2}\left[1 - \left(1 - \frac{M_t}{M_\infty}\right)^{2/3}\right] - \frac{M_t}{M_\infty} = k_t, \quad (30)$$

where $F_t$ is the fraction of bioactive species released at time $t$, $M_t$ is the amount released at time $t$, and $M_\infty$ is the amount released at infinite time [20, 38–45].

## 7. Failure Release

Experiments on the modified polymer or sulphur-coated urea granules (PSCU) conducted by Raban [46] revealed the main processes occurring during the failure release mechanism. The release process starts as water vapours penetrate through the coating. The rate of water penetration is defined by the driving force (vapour pressure gradient), the coating thickness, and features of the coating material. The water vapours condense and dissolve the fertilizer, thus causing a buildup of internal pressure inside the coated granule. The increase of internal pressure above a threshold value is likely to cause rupture of the coating (in contrast to the case of diffusion when the coating resists the pressure). The destruction of the coating leads to instantaneous release of the fertilizer.

Zaidel [47] analysed the forces involved during water penetration into a single granule and the rate of pressure buildup in it, from which it was possible to develop an expression for the time of "burst" or rupture ($t_b$) of a single coating (membrane):

$$t_b \cong \frac{r_0 l_0 Y}{P_h \Delta\pi M}, \quad (31)$$

where $r_0$ is the granule radius, $l_0$ is the coating thickness, $Y$ is the yield stress of the coating (Pa), $P_h$ is the water permeability of the membrane ($\text{cm}^2\,\text{day}^{-1}\,\text{Pa}^{-1}$), $\Delta\pi$ is the gradient of osmotic pressure across the membrane (Pa), and $M$ is Young's module of elasticity of the coating (Pa).

## 8. CRFs Release Properties

Characterization of release from a given SRF/CRF is one of the most important steps in assessing the efficacy of a given fertilizer. Trenkel and IFI Association [10] provides a partial list of methods used by several manufacturers of coated fertilizers to assess the release of different SRFs/CRFs. Tests performed at temperatures ranging from 2°C to 60°C at varying sampling frequencies are reported.

Release characteristics may be attributed to both physical effects (such as reduced diffusion rates in soils, moisture and temperature fluctuations [48]) and chemical effects (pH changes, root excretion) as well as to the action of microbes on biodegradable materials (UF, sulphur coating, waxes, etc.). This implies that a correlation between laboratory tests and release rates obtained under field conditions is required in order to achieve the highest NUE with the CRFs [7]. Release curves are the best common methods used in the characterization of nutrient release from the CRF formulation as seen in Figures 1–4 above.

Despite the release curves, several other parameters are known to be used in evaluating the properties of a particular CRF formulation such as water permeability [49] swelling ratio, and dissolution rate [50] which account for release behaviour. Others include zeta potential (ZP) and particle size [51, 52] together with morphology and thermal degradation properties [53].

## 9. CRFs and Biodegradability

Biodegradability means that a material has the proven capability to decompose in the most common environment where the material is disposed within 3 years through natural biological processes into nontoxic carbonaceous soil, water, carbon dioxide, or methane.

*Partial Biodegradation*. This relates to the minimal transformation that alters the physical characteristics of a compound while leaving the molecule largely intact. In other words, it refers to the alteration in the chemical structure of a substance, brought about by biological action, resulting in the loss of a specific property of that substance. Partial biodegradation is not necessarily a desirable property, since the intermediary metabolites formed can be more toxic than the original substrate. Therefore, mineralization is the preferred aim is such cases.

*Complete Biodegradation*. This occurs when the molecular cleavage is sufficiently extensive to remove biological, toxicological, chemical, and physical properties associated with the use of the original product, eventually forming carbon dioxide and water.

*Readily Biodegradable*. This is an arbitrary classification of chemicals which have passed certain specified screening tests for ultimate biodegradability; these tests are so stringent that it is assumed that such compounds will rapidly and completely biodegrade in aquatic environments under aerobic conditions.

*Inherently Biodegradable*. This is a classification of chemicals for which there is unequivocal evidence of biodegradation (partial or complete) in any test of biodegradability.

Despite the fact that an understanding of biodegradability is vital, the questions remain to be how biodegradable is the material? According to Han et al. [49], the test of biodegradability in CRF formulation is achieved by cutting CRF films into small squares such as 3 × 3 cm. Each specimen is then weighed and placed in agricultural soil (in a pot); subsequently, the pots are exposed to ambient conditions for 50 days. Variations in film morphology and disintegration time are then recorded as a test for biodegradability [49].

Similarly, terms like "environmentally friendly," "environmentally preferable," and "environmentally responsible" have been used to describe a material produced by biodegradable starting materials. In that case, one can freely use these terms interchangeably without distorting the meaning of the biodegradability concept.

## 10. Composition of CRF' Formulations

Basically most CRFs may contain among others the following components.

*10.1. Polymer Solution.* A number of polymers have been used in fertilizer coating; such polymers could be thermosetting, thermoplastic, or biodegradable ones. Some of the common thermoset polymers include urethane resin, epoxy resin, alkyd resin, unsaturated polyester resin, phenol resin, urea resin, melamine resin, phenol resin, and silicon resin. Among them, urethane resin urethane is very commonly used [1]. In addition, polyacrylamide is known to reduce soil erosion and so in this review we recommend that more studies should be conducted for its advanced use in CRFs [2, 54]. Thermoplastic resins are not very commonly used in practice because they are either not soluble in a solvent or make a very viscous solution which is not suitable for spraying; however, polyolefin is used in the art for coating the fertilizer granules. Biodegradable polymers are naturally available and so they are known to be environment friendly because they decompose in bioactive environments and degrade by the enzymatic action of microorganisms such as bacteria, fungi, and algae and their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. However, both synthetic and natural polymers containing hydrolytically or enzymatically labile bonds or groups are degradable [25]. In the field of agriculture, the use of polymers is only limited by their relatively high cost, which has restricted their use mainly in light and medium soils with high sand content [55]. Therefore, in this review we have decided to concentrate on some natural biopolymers that are useful in CRF practices, for instance, natural rubber which was used by Hanafi to develop CRFs formulations [56].

*10.1.1. Natural Polymers in CRFs Practices.* Hitherto, natural polymers have been used to replace synthetic ones for the reason that they are inexpensive, they can control soil erosion [54], and they have low toxicity and excellent biodegradability [57]. Basically, natural polymers are more superior to the synthetic polymers owing to their highly organized macroscopic and molecular structure which in turn adds to their strength and biocompatibility [57]. There are three basic types of natural polymers widely used in the controlled release delivery systems. These are neutral, for example, hydroxypropylmethylcellulose (HPMC), cationic, for example, chitosan, and anionic polymers, for example, $\kappa$-carrageenan and sodium alginate. Several natural polymers including a few lists below have been used in the design of controlled release formulations of drugs and fertilizers as described hereunder.

*Chitosan*. This is a cationic polysaccharide composed of linear copolymers of glucosamine and *N*-acetyl glucosamine resulting from partial deacetylation of chitin obtained from crustacean shells. The natural rich sources of chitosan include chitin of invertebrates, insects, and yeasts [58]. Researches indicate that complexes formed between chitosan with bioactive compounds and other polymers are useful in modifying the release profile characteristics in different preparations [57]. In fact, it is found to provide first order release kinetics especially when particle size of less than 75 micron was used [58]. Several studies have been conducted using chitosan nanoparticles; the findings reveal that it is possible to intercalate NPK fertilizers into chitosan nanoparticles prepared by polymerizing methacrylic acid [59]. Interestingly, chitosan nanoparticles obtained showed spherical shapes and uniform sizes of approximately 78 nm [59].

The mechanism to optimize the incorporation of the N, P, and K elements into the designed chitosan nanoparticle is yet to be described [59]; this creates a gap for further research. Jamnongkan and Kaewpirom [50] reported CRF hydrogels prepared from chitosan, polyvinyl alcohol, and polyvinyl alcohol/chitosan, using glutaraldehyde as a crosslinker. The synthesized CRF hydrogels exhibited high swelling ratio [50]. Wu and Liu [60] managed to prepare chitosan-coated nitrogen, phosphorus, and potassium compound fertilizer with controlled-release and water-retention (CFCW) capacity using inversion suspension polymerization [60]. Besides, the CFCW synthesized possessed excellent water retention capacity and thus, can potentially be considered as a suitable formulation for both agricultural uses as well as for use in the arid and desert environments reclamation endeavors.

*Xanthan Gum*. This is a high molecular weight, water soluble, anionic-bacterial heteropolysaccharide; it is a hydrophilic polymer, biocompatible, and inert and thus it provides time-dependent release kinetics [57]. Xanthan gum (XG) is used as a rheology modifier and is derived as a result of microbial fermentation of glucose from the bacterial coat of *Xanthomonas campestris* [57]. As a matter of fact, the applications of XG in the CRFs industry are less common however, findings prove that XG matrices exhibit quite consistent higher ability to retard drug release for controlled-release formulation [61]. This calls for further investigations on its use in CRFs.

*Carrageenan*. This is a naturally occurring high molecular weight anionic gel-forming polysaccharide extracted from certain species of red seaweeds (Rhodophyceae) such as *Chondrus crispus*, Eucheuma, *Gigartina stellata,* and Iridaea [57]. It is made up of the repeating units of galactose and 3, 6 anhydrogalactose. Depending on the different degree of sulfation, they are classified into various types: $\iota$-(monosulfate), $\kappa$-(di-sulfate), and $\lambda$-carrageenan (tri-sulfate). $\iota$- and $\kappa$-carrageenan forms gel while highly sulphated $\lambda$-carrageenan is a thickening agent and does not form gel, which influences their release kinetics [57]. The integrated method for production of carrageenan and liquid fertilizer

from fresh seaweeds is known [62]. In their work, the fresh biomasses of seaweeds *Kappaphycus alvarezii* were crushed to release sap which was then used for extraction of *κ-carrageenan*. The extract was found to be a superior raw material for production of liquid fertilizer after suitable treatment with additives. A novel biopolymer-based superabsorbent hydrogel synthesized after graft copolymerization of acrylic acid onto kappa-carrageenan backbones is reported to have been successfully researched [26]. Release studies revealed that Kappa-carrageenan is effective in minimizing burst release (bust effects versus tailing effects); in fact the burst release is found to depend highly on the degree of cross-linking and the mesh space available for drug diffusion [63].

*Pectin*. It is a methoxyester of pectic acid found in the higher plants cell walls [57, 58]. Certain fruits such as apple, quince, plum, gooseberry, grapes, cherries, and oranges also are known to contain pectin [57]. Little is known about pectin based CRFs; however, a pectin-based hydrogel used for removing $Cu^{2+}$ and $Pb^{2+}$ ions from water and wastewater and in the release of phosphate, potassium, and urea has been reported. The finding revealed that the pectin based hydrogel is effective in conserving water necessary for absorption by horticultural plants [64]. Non-Fickian mechanism was seen to control the release process of fertilizer nutrients from the hydrogels.

*Tamarind Seed Polysaccharide (TSP)*. Tamarind seed polysaccharide (TSP) is a galactoxyloglucan (a monomer of mainly three sugars-galactose, xylose and glucose in a molar ratio of 1 : 2 : 3) isolated from seed kernel of *Tamarindus indica* [57]. Being a natural biopolymer TSP is nontoxic, biocompatible and cheap agro-based material for use in CRFs practices giving zero order release kinetics [58].

*Mimosa pudica Seed Mucilage*. Mimosa mucilage is known to act as a matrix forming agent for sustained delivery of formulations [57]. According to Kumar and Gupta, Mimosa mucilage biopolymer exhibited bioadhesion time of 10 h and more than 85% release of drug in 10 h [58]; however, its use in CRFs industry is yet to be exploited.

*Leucaena leucocephala Seed Polysaccharide (LLSP)*. LLSP is a galactoxyloglucan hydrophilic gum isolated from seed kernel of *L. leucocephala*. In the controlled release art, LLSP has been used for controlled release of water-soluble plus water-insoluble drugs [57]. Intercalation of nitrogen fertilizer into the *L. leucocephala* residues under different moisture situation indicated that N content in soil released from residues increased with the time. Relatively higher amount of N release was observed in *L. leucocephala*, although the rate of N release was more with low N concentration residues [65]. In fact, this biopolymer is known to be a suitable natural disintegrant thereby being potentially useful in solid dispersion formulations for modifying rheological flow properties. It is also useful as suspending and emulsifying agent owing to its pseudoplastic and thixotropic flow patterns [66].

*Guar Gum*. This is a nonionic naturally occurring, hydrophilic polysaccharide extracted from the seeds of *Cyamopsis tetragonolobus* and is used as binder and disintegrant [57]. It acts as the release-retarding polymer which follows a first-order release kinetic. *C. tetragonolobus* has been confirmed to be a suitable excipient for controlled release practices, although its use in CRFs is not clear and so opening door for further researches [58]. Findings revealed that increased gum concentration raises the swelling index value which is ideal for slow release kinetics [57, 67]. In addition, Alginate which is a natural polysaccharide obtained from marine brown algae and seaweeds and produced by some bacteria such as *Pseudomonas aeruginosa* or *Azotobacter vinelandii,* could be used in the same way. In a point of fact, Alginate is a hydrophilic salt of alginic acid consisting of two uronic acids, $\beta$-D-mannuronic acid (M) and $\alpha$-L-glucuronic acid (G).

*Terminalia catappa Gum (TC)*. It is a gum exudate obtained from *Terminalia catappa* Linn. It is a natural release retarding polymer. The drug release retarding behaviour of TC gum is well studied [68, 69]. Kumar et al. [69] demonstrated the excellent swelling properties of TC gum in water and its ability to sustain the release of dextromethorphan hydrobromide from matrix tablet. Therefore, tablet formulations containing TC gum as an excipient may ensure the utility of the TC gum in controlled drug delivery systems of sparingly water-soluble, low molecular weight drug substance. Nevertheless, how suitable TC gum is in CRFs is not clear.

*Gellan Gum*. This is a hydrophilic, high molecular weight, anionic deacetylated exocellular polysaccharide gum isolated as a fermentation product from a pure culture of *Pseudomonas elodea*. It consists of a tetrasaccharide repeating unit of one $\beta$-D-glucuronic acid, one $\alpha$-L-rhamnose, and two $\beta$-D-glucose residues. On top of that, Grewia *gum* is a natural, hydrophilic polysaccharide obtained from the inner bark of the tree; *Grewia mollis* is known to hydrate on contact with water and swells to form a highly viscous dispersion making very suitable for CRFs [50].

*Mucuna Gum*. Mucuna gum is a biodegradable, amorphous polymer composed of mainly D-galactose along with D-mannose and D-glucose and isolated from the cotyledons of plant *Mucuna flagillepes*. Interestingly, studies show that formulations without crosslinking showed the fastest drug release [53]. This signifies that Mucuna based CRFs would exhibit similar features.

*Gum Copal (GC)*. It is a naturally occurring hydrophobic resin isolated from the plant *Bursera bipinnata* and follow zero order release kinetics. To add more, Gum dammar (GD) which is a GC sister is also anticipated to exhibit similar release kinetics as in GC. Primarily, GD is a naturally occurring hydrophobic gum obtained from plant *Shorea wiesneri*.

*Karaya Gum*. It is a hydrophilic naturally occurring gum obtained from *Sterculia urens* and composed of galactose, rhamnose, and glucuronic acid. It swells in water and is thus used as release rate controlling polymers in different formulations.

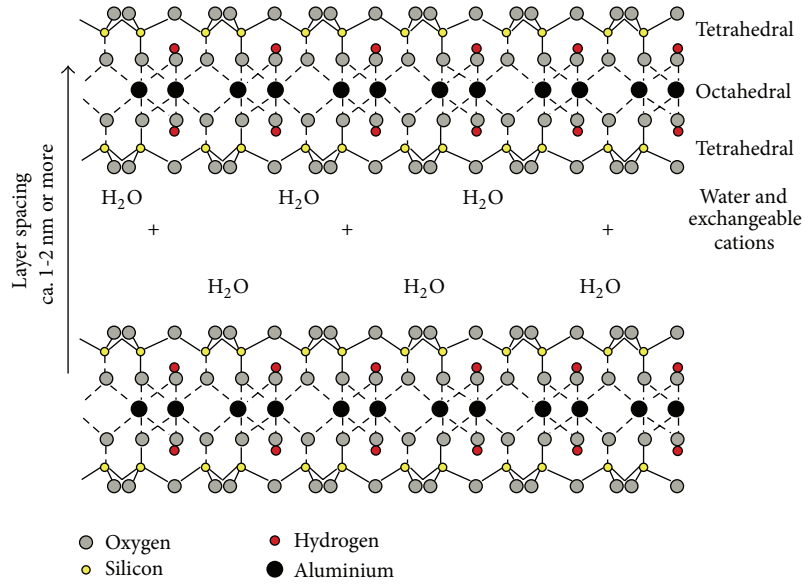



Figure 7: Structure of clay minerals.

Furthermore, Kumar and Gupta [58] provide an additional list of natural polymers used in controlled release systems including the following.

*Rosin*. a clear, pale yellow to dark amber thermoplastic resin present in oleoresins of the tree *Pinus roxburghii* and *Pinus taeda* belonging to the family Pinaceae. Rosin acts as a hydrophobic matrix forming agent for development of controlled drug delivery systems. It could be used as a binding agent and coating and matrix forming agent and so can be utilized as microencapsulating agent [70].

*Gum Acacia*. It is from stems of the *Acacia arabica* tree and can be used as encapsulating agent [71]. Locust bean gum provides excipient which gives sufficient mucoadhesive applications [72–74]. Other gums in a list include Khaya gum from Khaya *grandifoliola* used as binding and coating agent [75–77], Tragacanth gum used for sustained release [58], Okra gum from *Hibiscus esculentus* used in the formulation of sustained-release [78], and *Hibiscus rosa-sinesis* mucilage used to improve binding efficacy and hence acting as release-retarding agent [79, 80]. Moreover, olibanum and its resin [81], gum copal and gum damar [82], fenugreek mucilage [83], and dika nut mucilage (*Irvingia gabonensis*) are as well known to be used as binding agents in the release formulations [84].

*10.2. Modified Clays.* Nanoclay is the most common nanoparticle which has been used to produce CRFs. The layered clays like montmorillonite and kaolinite are made of high aspect ratio nanolayers. Large surface areas and reactivity of nanolayers are much greater than those of micrometre size materials. Also, their surfaces and interfaces provide an active substrate for physical, chemical, and biological reactions. Because of these features, nanolayers could be a suitable carrier or reservoir of fertilizers. Mechanisms which are involved in interaction between clay and organic materials depend on some factors like clay type, functional groups of organic material, and physical or chemical properties of organic material. For example basic molecules bond strongly to montmorillonite unlike anionic molecules which exhibit much weaker interactions. Similarly, benzoic acid or anionic species are adsorbed on the edge face of clay (cationic or crystal violet particles) after being adsorbed on the basal plane [1]. Basically, modification of clay can be achieved in many ways and different types of modified clay are named according to the methods followed such as pillared layered clays, organoclays, nanocomposites clays, acid and salt-induced modified clays, and thermally and mechanically induced modified clays. The use of each modified clay types given above, preparation, and their application in nano-CRFs are given by Basak et al. [85].

*10.2.1. Organoclay Chemistry.* Characteristically, clay minerals are natural materials with particle size $<2\,\mu$m. Smectites, classified as 2 : 1 phyllosilicate clays, have a crystal lattice unit formed by one alumina octahedral sheet sandwiched between two silica tetrahedral sheets (Figure 7). The ion substitution or the site vacancies at the tetrahedral and/or octahedral sheets gives rise to a negatively charged surface. The exchangeable cations between the layers compensate the negative charge and may be easily exchanged by other metal cations, explaining the high ion exchange capacities of these minerals (70–120 meq/100 g). Due to this crystalline arrangement, smectites are able to expand and contract the interlayer while maintaining the two-dimensional crystallographic integrity. The interlayer between units contains positive cations and water molecules [86].

On the other hand, kaolinite, the main constituent of kaolin, is made up of tiny, thin, pseudohexagonal, flexible sheets of triclinic crystals with a diameter of 0.2–12 $\mu$m. The cation exchange capacity of kaolinite is considerably less than that of smectite in the order of 2–10 meq/100 g, depending on the particle size, but the rate of the exchange reaction is rapid, almost instantaneous [87]. Kaolinite adsorbs small molecular substances such as lecithin, quinolone, paraquat, and diquat. The adsorbed material can be easily removed from the particles because adsorption is limited to the surface of the particles (planes, edges), unlike the smectite where the adsorbed molecules are also bound between layers. This adsorption behaviour influences researchers to investigate kaolin as a vehicle for bioactive compounds and hence creating widespread pharmaceutical application of kaolin group of minerals as it is with smectites [88].

Properties such as colloidal particle size, crystalline structure, high specific surface area, charge, and swelling capacity confer on smectites and kaolin optimum rheological behaviour and excellent adsorption capacities for inorganic and organic substances such as drugs. In particular, the electrically charged surface of clay controls the interaction with other environmental ions, molecules, polymers, microorganisms, and particles. These processes have various technological applications such as drug delivery systems and controlled release fertilizers.

*10.3. Other Components.* Several other ingredients are known to compose CRFs formulations, namely, crosslinkers such as glutaraldehyde [50] and methylene-bisacrylamide (MBA) [89]; fertilizer nutrients such as urea and ammonium nitrate and initiators such as azobisisobutyronitrile (AIBN) [56], ZnO [56], and ammonium persulphate (APS) [89] have been used to create polymer before crosslinking. In addition to that, surfactants such as sodium octadecyl phosphate and sometimes a dispersion medium such as cyclohexane (which is normally used to disperse surfactant molecules) are also known in the release formulation practices [22]. In fact, different surfactants have been used in CRFs designs and the commonly used ones include nonionic surfactant molecules [90].

## 11. Polymer/Clay Superabsorbent Composites

According to Ekebafe et al. [23], the polymer-clay superabsorbent composites have been of great interest to researchers due to their comparative low production costs and high water absorbency. Apt superabsorbent composites by graft copolymerization reaction of acrylic acid (AA) and acrylamide (Am) on attapulgite micropowder using N, N-methylene bisacrylamide (MBA) as a crosslinker, and ammonium persulphate (APS) as an initiator in an aqueous solution are reported by the author. In fact, Ekebafe et al. describe acrylamide as a kind of nonionic monomer possessing good salt resistant performance and so a suitable raw material for superabsorbent synthesis [23]. In addition, attapulgite is described as a good substrate for superabsorbent composite materials due to its aluminosilicate layers with reactive surface hydroxyl groups.

## 12. Conclusion

Regardless of being widely used, fertilizers particularly nitrogenous ones by virtue of their high nitrogen content (≅46%) and somewhat low cost of production, are associated with up to 60% to 70% loss of the nitrogen being applied owing to ammonia produced through hydrolysis of say urea by soil urease ($NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$). Fundamentally, due to surface runoff, leaching, and vaporization, the utilization efficiency or plant uptake of urea, for example, is generally below 50% thereby escalating fertilization expenditure per season and reducing crop productivity. Such drawbacks related to the use of nitrogenous fertilizers could be corrected by amending conventional nitrogenous fertilizers with suitable excipients in order to manufacture CRFs so as to improve FUE by plants and minimize the losses thereby reducing repeated fertilization expenditure per season and maximizing crop yields. CRFs reduce the demand for short-season manual labour obligatory during critical periods, reduce stress and specific toxicity (as a result of synchronizing nutrient release with plants' demands), increase availability of nutrients and supply of nutrient forms preferred by plants, and augment synergistic effects between nutrients and plant roots. In that view point, it is worth noting that researchers ought to design nano-CRFs by using natural excipients materials to come up with efficient, effective, reliable, and cost-effective CRFs formulations based on the prevailing resource limitations thereby minimizing food crisis and other challenges facing crop production. Essentially, scientists should anticipate mending agronomic returns through scientific novelties; the motive behind this must be geared towards researching, innovations, and commercialization of the CRF products.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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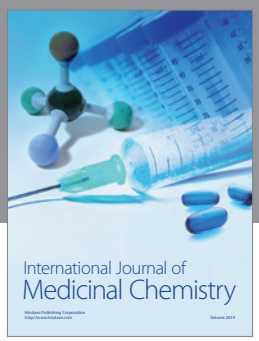
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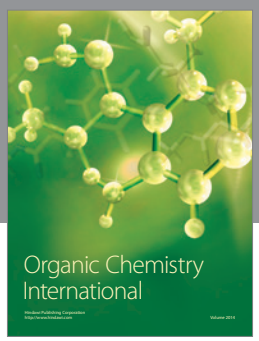
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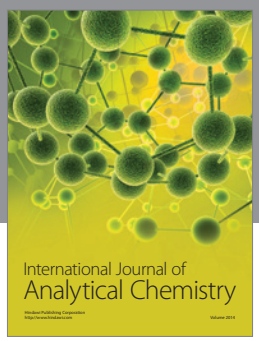
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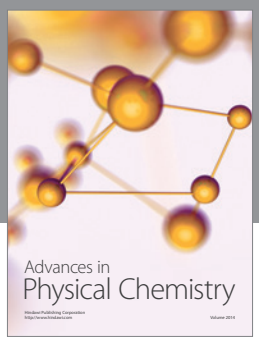
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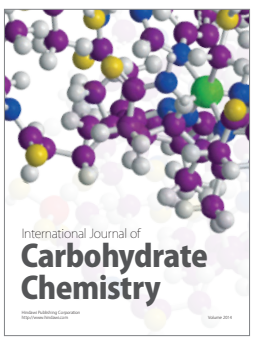


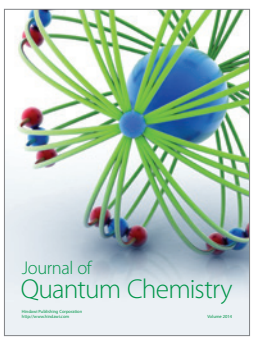












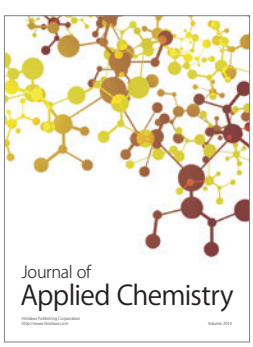


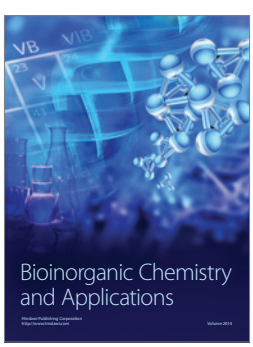




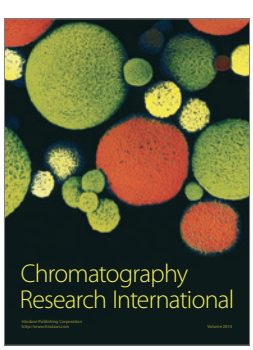




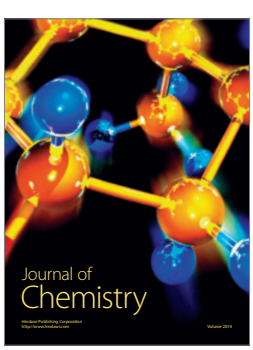














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