Controlled release of microcapsule fertilizer using ethylene vinyl acetate polymer

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Introduction

Controlled release fertilizers (CRFs) are now the most widely used fertilizers in the nursery industry for container–grown plants. A fundamental motivation for the development of CRFs has been the goal of delivering nutrients to plants at a rate that closely approximates plant nutrient demand over an extended period (Goertz 1993, Oertli et al. 1962b). Fertilizers with this ability can provide many benefits to agriculture, such as greater nutrient use efficiency, reduce nutrient leaching as compared to liquid fertilizer (Bunt 1988), better plant growth and quality, lower labor costs, and reduced fertilizer runoff pollution (Oertli et al. 1962b, Goertz 1993, Shaviv et al. 1993). A number of slow release fertilizers have been developed during the past decades. Generally there are three types of CRF fertilizers. The first major category of such fertilizers is accomplished by means of chemically controlled releasing products, such as urea-formaldehyde and polyphosphates. The release of such kind of slow release fertilizers is controlled by degradation rate, which in turn is affected by various factors, such as molecular weight of the polymer, pH, temperature, ions and microorganisms in the soil, etc.

Another way of regulation in release of fertilizer is coating fertilizer by some inert materials. The release of the fertilizer is controlled by diffusion through the shell. The coating materials used should be inexpensive and exhibit a good coating property. The type of coating is responsible for the mechanism of release of elements from encapsulated fertilizer (Tomaszewska et al. 2002). At present, CRF coating materials composed of either sulfur or polymeric substances or a combination of both (Goertz 1993). Polymer coated fertilizers (PCFs) are now the most sophisticated and advance means of controlling nutrient release and fertilizer longevity (Goertz 1993).

Matrix type formulation constitute is the third major category of slow or controlled release fertilizers due to simple fabrication. The active ingredients are dispersed in the matrix and diffuse through the matrix continual or intergranular openings, that is, through pores or channels in the carrier phase. Various materials may be used to synthesize the matrix phase in which the fertilizer is dispersed. Natural or synthetics resins (various waxes) and natural or synthetics polymers (starch, cellulose derivatives polyolefines and polydiolefines and their copolymers) were used in industrial practice (Hepburn et al. 1987). However, the mechanism of release from the matrix phase system is still unclear.

The objective of this study was to prepare some controlled-release micronutrient fertilizers using different polymeric materials. The release pattern of Fe ions in water was also evaluated.

Materials and Methods

The materials applied were Ethyl Cellulose (Asetifine Co., Germany) (EC), Glycerol Mono Asetearate (Merck Co. Germany) (GMS), Compritol 888 ATO (Gottefosse Co., France) (Compritol), Avicel (FMC Co., America), Lactose (Meggle Co., America), ferrous sulfate (Merck Co., Germany), Ethylene Vinyl Acetates (Aldrich Co., Germany) (EVA) and Carbon Tetrachloride (Merck Co., Germany). The microcapsules were prepared by extrusion/spheronization technique.

To make GMS and Compritol microcapsules, adequate powders of GMS or Compritol polymer, Avicel, Lactose and ferrous sulfate were mixed by a tumbler blender. Then, distilled water was added (65% wt.) drop by drop and stirred to provide a wet mass. This mass was passed through a mesh sieve and than spheronized for 10 minutes in a spheronizer (Sepahkar Co, Iran). The obtained microcapsules were oven dried at 25°C and sieved for separation of the 0.8-1.18 mm fraction. To make EC microcapsule, Avicel and ferrous sulfate were mixed for 2 minutes by a tumbler blender. Then, the powder mixture was wetted by an alcoholic solution of EC (175μg/ml). The wetted mass was extrudated and spheronized and microcapsules were dried in an oven. Table 1 shows the formulation of microcapsules.

Table 1. Microcapsule composition (g per 100 g of pellets)

Formulation	Avicel (g)	Lactose (g)	FeSO4.7H2O (g)	GMS (g)	EC (g)	Compritol (g)
GMS	37.5	7.5	5	50	-	-
Compritol	37.5	7.5	5	-	-	50
EC	76.9	-	5.1	-	18	-

Three g of 0.8-1.18 mm microcapsules were transferred to vessels of dissolution tester device (PHARMA TEST PTZWS3) with 750 mL of 25°C distilled water and the medium was stirred at 50 rpm by a paddle. At predetermined time intervals, samples (10 mL) were taken from the medium and analyzed by atomic absorbtion method (Perkin Elmer AA200) for determination of Fe concentration in solution. The medium volume was kept constant by adding 10 mL distilled water. All fertilizers release kinetics data were fitted to Higuchi model ($Q=kt^{1/2}$) (Higuchi 1963), Sinclair & Peppas ($Q=kt^{n}$) model (Sinclair et al. 1984) and first-order kinetic model ($Ln (Q_0-Q_t) =Ln (Q_0)-k t$) (Kochba et al. 1990). In all models, Q is the concentration of Fe ion (mg/L) in the dissolution vessel at time t, Q_0 is concentration of Fe when all fertilizer release to the water and k is a constant. To achieve the slower release rate of Fe, Compritol polymer microcapsules were coated by polymer. Microcapsules were dipped in the Ethylene Vinyl Acetates solution (50μg/ml of Carbon Tetrachloride) and then dried at room temperature. This treatment was repeated until the percentage of coating was reached to about 10% wt. These coated microcapsules are tested for Fe ions release.

Results and Discussion

Figure 1 shows release pattern of EC, GMS and Comp microcapsules. It was clear that the release of Fe^{+2} from the Comp microcapsules is very slower than that of EC and GMS. By increase of percentage of EC or GMS polymers in their formulations or by polymer coating may improve the release pattern from these microcapsules. Hence the microcapsules including Compritol 888 ATO polymer were selected for longer experiment. It is very important to reveal the mechanism governing the release of fertilizers in the dissolution medium. So release data for three types of microcapsule fertilizers were fitted to different models. The results have been shown in Table 2. It is observed that Higuchi formula has been fitted better than other kinetic models as it is based on the release from a matrix network (Sinclair et al. 1984). Al-Zahrani (2000) showed that modified hyperbola formula gives the best fit for describing the release data of different fertilizers used in his work. Figure 2 shows that Compritol microcapsules have released about 90% their micronutrient after 168 hours or about 7 days. The release rate of nutrients in soil is slower than in the water, because the release mechanism of a nutrient from a matrix structure consists of diffusion of water molecules to the matrix pores, dissolution of nutrient salts and then nutrient release. Oertli and Lunt (1962a, 1969b) investigated release patterns of PCfs in beakers of water (water elution) as well as in columns of soil or sand. Their results showed that over the same time period, total nutrient release was twice as great for a PCF in water than for the same PCF in sand or soil columns.
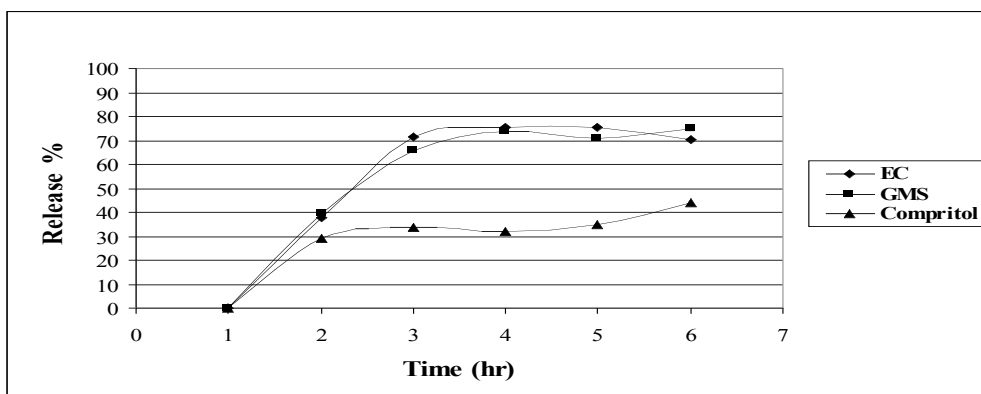
Figure 1: Release pattern of Fe from EC, GMC and Compritol microcapsules in distilled water

Table 2: Curve fitting results of the release data of the three types of microcapsule fertilizer

Polymer	Higuchi model $Q=kt^{1/2}$		Sincleir & Pappas model $Q=kt^n$			First-Order kinetic model $Ln(Q_0-Q_t)=Ln(Q_0)-kt$	
	$k(mg.h^2/L)$	r^2	$K(mg.h^{1}/n/L)$	n	r2	$k\ (h^{-1})$	r^2
EC	56.78	0.86	65.04	0.39	0.69	0.35	0.74
GMS	55.76	0.92	64.30	0.38	0.83	0.35	0.56
Comp	9.66	0.87	13.65	0.20	0.68	0.13	0.58
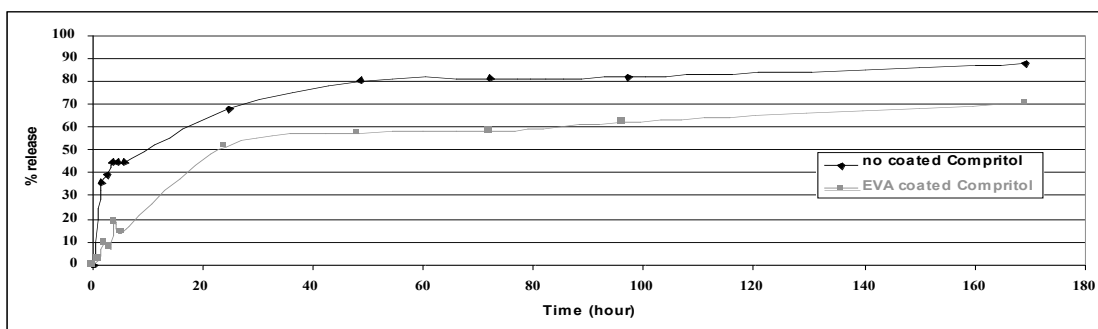
Figure-2: Release pattern of Fe from Comp microcapsules with EVA coating and without coating

They also speculated that PCF membrane characteristics may be altered in soil condition. Liang et al. Liang et al. (2007) observed that release of N, K and P from controlled release granules with a superabsorbent composite coating, was very slower in soil than in water. Also, based on Cabrera theory (Cabrera 1997), diffusion water vapor to the matrix structure causes existence of nutrient in the soil, so the release in the soil is longer. Hence, Comp microcapsules may have a good performance in the soil. Many factors influence CRFs nutrient release. The coating with EVA polymer caused to more decrease the release of Fe^{+2} from microcapsules. Figure 2 shows that after 24 and 48 hours microcapsules without coating have released 70% and 80% of their ferrous sulfate, respectively while EVA coated microcapsule have just released 51% and 58% of those, respectively. Also at the first 5 hours, release from coated microcapsule is slower and more regulated that no coated microcapsules and along this interval, they have released about 50% of their nutrient salt. The reason may be related to this fact that, at initial hours of experiment, the ferrous sulfate molecules which have placed on the surface or near the surface of non-coated fertilizers, contact with water and so dissolve very fast and easily. After this stage, for release of deeper nutrient salts, water must be diffused inside of matrix network and then nutrient solution

diffuses outside matrix. By polymer coating, release of surface nutrients is limited and the release rate becomes more slowly.

Conclusion

The results showed that EVA coated microcapsules with matrix structure of Compritol 888 ATO, can slowly release Fe ions in water medium within 7 days. So, it seems that these capsules would have good controlled release properties in the soil.

Acknowledgments

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