



UNIVERSITI PUTRA MALAYSIA

**FORMULATION AND EVALUATION OF CONTROLLED-RELEASE
DIURON AS PRE-EMERGENCE HERBICIDE**

NORIDA BT MAZLAN

FP 1999 22

**FORMULATION AND EVALUATION OF CONTROLLED-RELEASE
DIURON AS PRE-EMERGENCE HERBICIDE**

By

NORIDA BT MAZLAN

**Thesis Submitted in Fulfillment of the Requirement for
the Degree of Master of Agricultural Science in the Faculty
of Agriculture, Universiti Putra Malaysia**

May 1999



ACKNOWLEDGEMENTS

Praise be Allah swt., upon His permission I could complete this thesis smoothly. Contributions of individuals and institution for the successful completion of this thesis are also acknowledged.

I would like to take this opportunity to express my deep appreciation and gratitude to Associate Professor Dr. Dzolkhifli Omar for his valuable advice, guidance, suggestions, encouragement and strong support throughout the research work. I would also like to express my thanks to Professor Rosli Mohamad and Associate Professor Dr. Rajan Amartalingam for serving as members of the supervisory committee.

Sincere thanks and appreciation to Associate Professor Dr. Kamaruzaman Sijam for letting me used his camera for specific purposes of this project. Appreciation also goes to staff of the Toxicology Laboratory for giving me the opportunity to carry out the project and making all facilities available to me. Special thanks are also extended to my friends Zahariman, Puteri Edaroyati, Neni Kartini, Mahrta, Suraya, Helen and David for their help and encouragement. Finally, I would like to take this opportunity to convey my deepest thanks and love to my mother for the loving support given to make me where I am today.

I want to express my sincere gratitude to the Malaysian people for the opportunity to accomplish this goal and the Universiti Putra Malaysia for the financial support to carry out the master programme.



TABLE OF CONTENTS

		Page
ACKNOWLEDGEMENTS.....		ii
LIST OF TABLES.....		vi
LIST OF FIGURES.....		vii
LIST OF PLATES.....		Viii
ABSTRACT.....		ix
ABSTRAK.....		xii
CHAPTER		
I	INTRODUCTION.....	1
II	REVIEW OF LITERATURE.....	4
	Pesticide Usage and Environmental Contamination.....	4
	Agrochemical Industries.....	6
	Weeds Control with Herbicides.....	6
	Controlled-release Formulation Pesticides.....	8
	Controlled-release Products.....	9
	Advantages of Controlled-release Formulation Pesticides..	11
	Concept of Controlled-release Formulations.....	12
	Release Mechanisms of Controlled-release Formulations.....	14
	Membrane-Moderated Diffusion Release Systems.....	15
	Release by Erosion.....	17
	Chemical Reactions Release System.....	17
	Controlled-release Formulation Encapsulation Polymers	18
	Encapsulation Within Alginate.....	19
	Encapsulation Within Starch Matrix.....	19
	Encapsulation Within Kraft Lignin.....	20
	Encapsulation Within Synthetic Organic Matrices.....	21
	Factors Influencing the Release of Active Agent.....	21
	Determination of Release Rate.....	22
	Effectiveness of Controlled-release Formulation.....	24
	Diuron.....	26
	<i>Paspalum conjugatum</i>	27
	<i>Diodia ocimifolia</i>	28
	Agricultural Waste By-Products (AWP).....	29
	Oil Palm Empty Fruit Bunch.....	29
	Sawdust.....	29
	Paddy Husk.....	30



III	PREPARATION OF ALGINATE-KAOLIN CONTROLLED- RELEASE FORMULATIONS OF DIURON AND DETERMINATION OF ITS RELEASE RATES.....	32
	Materials and Methods.....	32
	Chemicals.....	32
	Equipment.....	33
	Preparation of Controlled-release Formulations of Diuron.....	33
	Analysis of Formulation for Content and Release Rate of Diuron.....	35
	Chromatographic Analysis.....	35
	Determination of Release Rate of Alginate-Kaolin Controlled-release Formulations of Diuron by Bioassay Technique.....	36
	Results and Discussion.....	38
	Production of Alginate-Kaolin Controlled-release Formulations of Diuron.....	38
	HPLC Analysis of Formulation for Content and Release Rates of Diuron.....	41
	Effect of Controlled-release Formulations of Diuron on Fresh Weight of <i>Brassica rapa</i> Seedling.....	44
	Effect of Alginate-Kaolin Controlled-release Formulations of Diuron on Mortality of <i>Brassica rapa</i> Seedlings.....	47
IV	PREPARATION OF ALGINATE AGRICULTURAL WASTE BY-PRODUCT CONTROLLED-RELEASE FORMULATION AND EVALUATION OF THEIR EFFECTIVENESS.....	57
	Materials and Methods.....	57
	Processing of Agricultural Waste Products.....	57
	Production of Alginate-AWP Controlled-release Formulations.....	58
	Analysis of Diuron Content and Determination of Its Release Rate from the Alginate-AWP Controlled-release Formulations.....	59
	Effectiveness of Alginate-Kaolin and Alginate-AWP Controlled-release Formulations.....	60
	Results and Discussion.....	61
	Production of Alginate-AWP Controlled-release Formulations.....	61
	HPLC Analysis of Alginate-AWP Controlled-release Formulation for Diuron Content and Determination of their Release Rates.....	63
	Efficacy of Evaluation of Formulated Controlled-release Formulations on <i>Paspalum conjugatum</i>	66

	Efficacy Evaluation of Formulated Controlled-release Formulations on <i>Diodia cymifolia</i>	67
V	CONCLUSION	71
REFERENCES	73
APPENDICES	82
	Appendix 1(a): ANOVA Table Tukey Grouping for Study (I).....	83
	Appendix 1(b): ANOVA Table Tukey Grouping for Study (II).....	89
	Appendix 2: Determination of Diuron Content and Release Rates of Controlled-release Formulations.....	91
VITA	92



LIST OF TABLES

Table		Page
1	Estimates of Agrochemical Market (RM Million) in Malaysia.....	8
2	Amount of Pesticide Needed for Effective Control Over Specific Periods...	14
3	Composition of Oil Palm Empty Fruit Bunch (EFB).....	30
4	Composition of Paddy Husk.....	31
5	Composition of the Three Different Ratios of Alginate and Kaolin.....	33
6	The Qualitative Scale for Visual Assessment.....	38
7	Water Loss and Fresh Weight Controlled-release Formulations Granules..	39
8	Percent of Diuron Released by Controlled-release Formulation in Methanol	41
9	Effect of Treatments on Fresh Weight of <i>Brassica rapa</i> Seedlings.....	45
10	Mortality of <i>Brassica rapa</i> After Treatments with CF and Controlled- release Formulations	50
11	Physical Characteristic of Alginate-AWP Controlled-release Formulations	62
12	Diuron Content in Alginate-AWP Controlled-release Formulations.....	64
13	Percent Mortality of 14 Days Old <i>P. conjugatum</i> Seedlings Sown at 1 and 2 Month After Treatments.....	67
14	Percent Mortality of 14 Days Old <i>D. ocimifolia</i> Seedlings Sown at 1 and 2 Month After Treatments	69



LIST OF FIGURES

Figure		Page
1	Relationships Between Level of Application and the Duration of Action for Conventional and Controlled-release Formulations.....	13
2	Slab Reservoir System	15
3	Sphere Reservoir System.....	16
4	Monolithic System	16
5	Chemical Structure of Diuron.....	26
6	Release of Diuron from Alginate-Kaolin Controlled-release Formulation into Distilled Water.....	43
7	Effect of Alginate-Kaolin Controlled-release Formulation on Fresh Weight of <i>Brassica rapa</i> Seedlings	46
8	Percent Mortality of <i>Brassica rapa</i> Seedlings at 1 and 3 WAT with Alginate-Kaolin Controlled-release Formulation.....	53
9	Percent Mortality of <i>Brassica rapa</i> Seedlings at 6 and 8 WAT with Alginate-Kaolin Controlled-release Formulation.....	54
10	Percent Mortality of <i>Brassica rapa</i> Seedlings at 9 and 10 WAT with Alginate-Kaolin Controlled-release Formulation.....	55
11	Percent Mortality of <i>Brassica rapa</i> Seedlings at 16 and 24 WAT with Alginate-Kaolin Controlled-release Formulation.....	56
12	Release Rate of AWP-AWP Controlled-release Formulation of Diuron....	65
13	Percent Mortality of <i>P. conjugatum</i> Seedlings by Alginate Controlled-release Formulation at 1 and 2 MAT.....	68
14	Percent Mortality of <i>D. ocimifolia</i> Seedlings by Alginate Controlled-release Formulation at 1 and 2 MAT	70



LIST OF PLATES

Plate		Page
1.	The Production of Alginate-Kaolin Controlled-release Formulations.....	34
2.	The Physical Structure and Size of the Controlled-release Formulations	40
3.	Diuron Peak on Histogram.....	42
4.	Ground and Sieved Agricultural Waste Products (AWP).....	58
5.	Alginate-AWP Controlled-release Formulation Floating in CaCl ₂ Solution.	62
6.	Alginate-AWP Controlled-release Formulation Ready for Use.....	63



Abstract of thesis submitted to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Agricultural Science.

**FORMULATION AND EVALUATION OF CONTROLLED-RELEASE
DIURON AS PREEMERGENCE HERBICIDE**

By

NORIDA MAZLAN

MAY 1999

Chairman : Associate Professor Dzolkhifli Omar, Ph.D.

Faculty : Agriculture

Controlled-release formulations of diuron were prepared in the laboratory using the concept of physical matrix utilizing sodium alginate and kaolin. The release rates of diuron from the formulations were determined by chemical assay and bioassay. In the chemical assay, using high performance chromatography with UV detector, significant differences in release rates between formulations were observed from 3 to 7 days after the granules were placed into distilled water. The formulation having a 1:1 ratio of alginate to kaolin with 1 mm granule size showed the fastest release of diuron while release from the 2 mm granules was slower. The release of diuron from the formulations reached a maximum level of 27% at 30 days after placement in water this same rate of release was maintained up to 60 days after the treatment. Increasing the proportion of kaolin to sodium alginate in the controlled-release formulation reduced the release rate of active agent.



Bioassays were conducted in the glasshouse to study the release rates of diuron using *Brassica rapa* seedlings as bioindicator. The controlled-release formulations showed slower release than the conventional formulation at the beginning of the treatments. At 3 weeks after treatment, there was no significant difference in the mortality of the seedlings between the conventional formulation and controlled-release formulations. However, the controlled-release formulations gave significantly higher seedling mortality compared to the conventional formulation at 16 weeks after the treatments. The same results were observed up to 24 weeks after the treatment when the controlled-release formulations caused between 40 to 70% mortality, while the conventional formulation treatment caused only 6% mortality. Among the controlled-release formulations, the AK-2 formulation (1:1, alginate to kaolin) was found to give the best control with the highest percentage mortality of the seedlings.

Controlled-release formulations of diuron were also prepared using the same ratio of 1:1 with alginate and agricultural waste products sawdust (SAW), oil palm empty fruit bunch (EFB) and paddy husk (PDH). Chemical assay showed 90% of the diuron was successfully incorporated in the granules in these formulations and similar rates of release were obtained when compared with the kaolin based controlled-release formulations. A significant increase in active agent released was observed between 3 to 7 days after placement in water. The release reached a maximum at 25 days, and subsequently was maintained at the same rate until 60 days. However, the release rates of agricultural waste product formulations were lower compared to AK-2.



The biological efficacy of the controlled-release and conventional formulations on *Paspalum conjugatum* and *Diodia ocimifolia* were evaluated in the glasshouse. No significant difference in mortality between the formulations was obtained with *P. conjugatum* at 1 month after treatment (MAT). However, significantly higher seedling mortality was observed with the controlled-release formulations, except the PDH formulation at 2 MAT. Similar results were obtained with *D. ocimifolia* and at 2 MAT all controlled-release formulations caused significantly higher seedling mortality of the compared to the conventional formulation. The controlled-release formulations gave 60-85% mortality compared to 40% shown by the conventional formulation.

Abstrak tesis yang di kemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan syarat untuk mendapatkan
Ijazah Master Sains Pertanian

**FORMULASI DAN PENILAIAN RACUN LEPASAN TERKAWAL DIURON
SEBAGAI RACUN HERBA PRACAMBAH**

Oleh

NORIDA MAZLAN

MEI 1999

Pengerusi : Profesor Madya Dzolkhifli Omar, Ph.D.

Fakulti : Pertanian

Formulasi racun lepasan terkawal diuron telah di hasilkan secara konsep matrik fizikal mengguna sodium alginat dan kaolin. Kadar perlepasan diuron dari formulasi berkenaan telah diuji secara kimia dan biologi. Kromatografi cecair bertekanan tinggi dengan pengesanan UV telah digunakan di dalam ujian kimia. Kadar perlepasan yang bererti telah di perolehi pada hari ke-3 dan ke-7. Pada hari ke-3, formulasi yang mengandungi nisbah 1:1 alginat dan kaolin (AK-2) dengan granul bersaiz 1 mm memberikan kadar perlepasan yang tertinggi manakala formulasi AK-1b memberikan perlepasan yang terendah. Perlepasan diuron dari formulasi alginat-kaolin mencapai tahap maksima pada hari ke-25 selepas direndam didalam air suling dengan melepaskan sebanyak 27% daripada jumlah keseluruhan diuron yang terkandung di dalam formulasi. Perlepasan diuron berterusan pada kadar yang tetap sehingga hari ke-60. Keputusan juga menunjukkan penambahan kaolin di dalam formulasi lepasan terkawal mengurangkan perlepasan bahan aktif.



Ujian kadar perlepasan secara biologi menggunakan anak benih *Brassica rapa* sebagai penunjuk telah dijalankan di dalam rumah kaca . Pada awal rawatan, formulasi lepasan terkawal memberikan kadar perlepasan yang perlahan berbanding formulasi lazim. Pada minggu ke-3 selepas rawatan, tiada keputusan yang bererti ke atas kematian anak benih berkenaan di antara rawatan formulasi lazim dengan formulasi lepasan terkawal. Bagaimanapun formulasi lepasan terkawal menunjukkan peratus kematian yang lebih tinggi berbanding formulasi lazim pada minggu ke-16. Keputusan ini berterusan sehingga minggu ke-24 selepas rawatan, di mana formulasi lepasan terkawal masih memberikan peratus kematian di antara 40 – 70% manakala formulasi lazim hanya menyebabkan 6% kematian. Di antara rawatan formulasi lepasan terkawal , formulasi AK-2 (1:1) didapati memberikan keputusan yang paling baik.

Formulasi lepasan terkawal berbahan sampingan dengan nisbah 1:1 telah di hasilkan dengan menggunakan alginat dan bahan buangan pertanian habuk papan(SAW), tandan kelapa sawit (EFB) dan hampas padi (PDH) mengganti kaolin sebagai pengisi. Ujian kimia menunjukkan 90% diuron telah berjaya diisi di dalam granul dan kadar perlepasan racun yang serupa telah diperolehi dengan kajian yang terdahulu. Perlepasan bahan aktif yang bererti didapati antara hari ke-3 hingga hari ke-7 rawatan. Perlepasan bahan aktif mencapai tahap maksima pada hari ke-25 dan ia berterusan pada kadar yang sekata sehingga hari ke-60. Didapati kadar perlepasan daripada formulasi bahan buangan pertanian adalah lebih rendah bila dibandingkan dengan formulasi AK-2.

Efikasi formulasi lepasan terkawal diuron dan formulasi lazim ke atas rumpai *Paspalum conjugatum* dan *Diodia ocimifolia* telah dijalankan di rumah kaca. Tiada kesan bererti ke atas kematian di antara semua rawatan terhadap *P. conjugatum* pada bulan pertama selepas rawatan. Bagaimanapun, pada bulan kedua, didapati peratus kematian yang bererti pada rawatan formulasi lepasan terkawal (kecuali formulasi PDH). Keputusan yang sama diperolehi pada rumpai *D. ocimifolia*. Pada bulan ke-2 selepas rawatan kesemua rawatan formulasi lepasan terkawal memberikan jumlah kematian yang bererti berbanding dengan rawatan formulasi lazim. Formulasi lepasan terkawal memberikan 60-85% kematian berbanding 40% daripada rawatan formulasi lazim.

CHAPTER I

INTRODUCTION

The rapid growing demand for food production stimulates research in the agricultural sector. Tropical areas are conducive for a high crop productivity due to the high levels of radiation, longer growing season and ample rainfall, but at the same time many of the world's worst weeds also flourish, making effective weed management essential for high yields. The use of chemicals for weed control is the 20th century technique. However, some herbicide treatments have led to soil erosion and water contamination. An effective approach in reducing the environmental loss of herbicide and providing more efficient weed control is through the use of controlled-release herbicide (Ishikawa *et al.*, 1977). Controlled-release formulation is also less phytotoxic on plants by 45% than the EC formulations (Flynn *et al.*, 1994). In rice, the control of *Echinochloa crusgalli* using controlled-release thiobencarb gave better yield than the conventional formulation (Omar and Mohamad, 1994).

Controlled-release formulation of pesticides are defined as depot systems which continuously release their toxic constituents into the environment over a specified period of time (Cardarelli, 1976). The principle of controlled-release was derived from pharmaceutical practices in the 1960's. In 1969, an ester of 2,4-D was formulated in natural rubber. This was the first long-term controlled-release formulation herbicide developed.



Since then many methods were developed to encapsulate the active agent in the polymer. Shasha *et al.* (1976) used crosslinking of starch xanthate to incorporate diazinon and butylate. Encapsulation of carbofuran by starch-urea-formaldehyde was used by Rajagopalan *et al.* (1995). Other polymers used include kraft lignin (Dellicolli, 1977), polyethylene film (Oh *et al.*, 1994) and calcium alginate (Barret and Logan, 1982; Hussain *et al.*, 1992; Gerstl *et al.*, 1994 and Mardi, 1994). Among the biopolymers used as an encapsulation agent, calcium alginate was widely studied. It was easy to study the release rate of the active agent due to the uniformity in size of the beads produced.

The research showed that controlled-release formulation gave good control of weeds over longer period of time, but the initial release of toxicant was slow. This leads to lower efficacy of weed control at the early stage. The filler to encapsulation agent ratio and type of filler have been associated with release rate of toxicant (Mardi, 1994) . In monolithic system of controlled-release formulation, kaolin is usually used as a filler. In Malaysia, there are abundance of the agricultural by products such as oil palm empty fruit bunch, paddy husk, cocoa husk, paddy husk and palm oil mill effluent which could be utilised as fillers. However, studies on the use of these materials as fillers are lacking.

In view of this, the objectives of this research were to prepare controlled-release formulations of herbicide and to evaluate the influence of the formulation composition and size of granules on the initial release and activity of the active agent. The use of agricultural by-products such as sawdust, oil palm empty fruit bunch and paddy husk as fillers were also included in this study. The release rates of the controlled-release formulations and their effectiveness as pre-emergence herbicide

were also determined. The pre-emergence herbicide diuron was used in these studies.

CHAPTER II

REVIEW OF LITERATURE

Pesticide Usage and Environmental Contamination

In 1945, research in Britain and United State resulted in the discovery of phenoxy herbicides, with products such as MCPA and 2,4-D for selective control of broad-leaved weeds (Brian, 1964). In the case of insecticides, DDT was first tested as a moth proofing material in 1939 and soon became the universal insecticide. Since then the use of pesticides has been widely adopted by farmers in developed and developing countries. It has contributed to increase food production in the world through reducing the damage cause by pests thus increase the yield. The pesticides also reduces the labour cost, thus increasing the labour efficiency. This has led to increase dependence on pesticides. It has also been reported that a decision to stop the use of crop protection chemicals in USA alone would reduce the total output of crops and livestock by 30% and increase the price of farm products between 50 to 70% (IAEA, 1994).

The increase in use of pesticides particularly the persistent ones has led to problems of environmental contamination. Nevertheless, pesticides show lower persistency in tropical soil region compared with those in the temperate. This was due to the organic matter content of less than 5% in tropical soil give little adsorption of pesticides and thus a high leaching potential into the environment.

Apart from leaching, environmental contamination from excessive use of pesticides could also occur through groundwater contamination and surface run-off. Herbicides and other agricultural chemicals have been detected in numerous rivers throughout the United States due to their widespread application for the last 20 years (Nielsen and Lee, 1987). Many formulations of pesticide also contain volatile organic compounds such as alkylbenzenes, chlorobenzenes and ketones. Thus, it is not surprising that some volatile organic compounds have been detected in surface water, groundwater, landfill leachates and coastal water (Battista and Connelly, 1989; Dupont *et al.*, 1990).

The unknown hazard of pesticides to the health of spray operator and consumer is another problem. In 1993, it was estimated that about 23% of 7.75 million workers in 1995 were engaged in the agricultural forestry and fishing sectors (Ministry of Human Resource Malaysia, 1993). These workers are at risk to pesticides exposure. The exposure to the pesticide could be occur through the contact with skin. The rate of pesticide absorbed through the skin is dependent on its solubility in both water and lipids, the area of skin in contact, the skin condition and location on the body and the duration of contact (Legaspi and Zenz, 1994). In Malaysia, over the period of 1979-1988, 40% of human poisoning cases reported were due to pesticides, of which paraquat poisoning accounts for 70% (Zainal Abidin, 1994). About 11% of the 6554 pesticides poisoning cases were reported to Government hospitals between 1989-1994 (Ministry of Health,1996).

Agrochemical Industries

Rapid growth of pesticide use for crop protection began in 1940's with the introduction of insecticides such as BHC, DDT and the phenoxy-acid hormone herbicides 2,4-D and MCPA. As technology advances and development progresses, many more new agrochemical are produced and introduced into the market. The British Agrochemical Association reported that in 1996, the world agrochemical market rose 3.6% to approximately US\$31.25 billion. North America accounted for the highest level of pesticides sales with 30.6%, followed by Western Europe with 26%, East Asia 22.5%, South America 11.9% and the rest of the world for the remaining 9%. Herbicides accounted for the biggest portion of pesticides sales with 48% of the world market followed by, insecticides 28% and fungicides 19% (Agrow, 1997).

In Malaysia, the agrochemical industries started in the early 1920's with the use of inorganic pesticides, followed by arsenic substrates and DSMA (Sahid, 1988). The market for agrochemical in Malaysia increases every year. Estimate of agrochemical market for pesticides in the year 1997 was RM 326 million with herbicides contributing 80% of the amount. A 4% growth was observed from the year 1996 to 1997 (MACA, 1998).

Weeds Control with Herbicides

Weeds are a common problem to crops. They compete with cultivated crops for soil nutrients, sunlight and water resources. Weeds have a wide adaptation to the

environment and grow faster than the crop plants. Aquatic weeds block the irrigation channels, retard fish production, harbour undesirable insects and hamper navigation.

Before the introduction of herbicides, weeds were controlled by hand weeding, cultural practices and mechanical methods. In the early 1940's, there was a shortage of manpower and increase in management cost. Subsequently, farmers preferred using herbicides to control the weeds.

Herbicides are applied in many ways such as spraying to the leaves, ground or the aquatic environment. They have activities such as selective and non-selective. The selective herbicides will only kill selected weed species, whereas the non-selective herbicides will kill all types of weeds. Herbicides usually act through contact or systemic action. The contact herbicide will act by killing the soft tissues that come into contact with it, whereas systemic herbicides are absorbed and distributed in the whole plant. The effect of the latter is slower and takes a longer time to kill the weeds.

Herbicides are the largest group of pesticides used in Malaysia (Tan, 1991). The herbicide usage in Malaysia increased at the rate of 4% from 1996 to 1997 (MACA, 1998). The market for pesticides continues to be dominated by herbicides that constitute about 77% of the total value (Table 1). Herbicides are used in oil palm, rubber and cocoa plantations as well as rice fields, horticultural plants and turf grasses.

Table 1: Estimates of Agrochemical Market (RM Million)# in Malaysia.

Crop Protection Chemicals	1993	1994	1995	1996	1997
Herbicides	200	210	220	227	245
Insecticides	39	41	43	47	52
Fungicides	13	14	15	16	17.5
Rodenticides	10	11	11	11	11.5
Total	262	276	289	301	326

#End-user value (From MACA Annual Report 1997/98)

Some of the important herbicides used in Malaysia include paraquat, 2,4-D amine, DSMA, diuron and glyphosate. The estimate value of herbicides import by Malaysia in 1995 was RM 31,708.00 million (Malaysian Agriculture Directory and Index, 1998). It was evident that herbicides will continue to be an important component of Malaysian agriculture as long as labour shortage makes manual weeding uneconomical.

Controlled-release Formulation Pesticides

Scientists have dealt with the problems of pest control by designing new and more potent agents. Enormous amounts of funds are required for the development of new biocides. However, use of these agents to produce the desired biological response is often inefficient, primarily because of the inability to deliver the agents to their targets at the precise time and in the optimum quantities required. Therefore, one of the alternative to improve the efficiency is by using controlled-release formulation. A controlled-release formulation delivery system is defined as a

combination of biologically active agent and excipient, usually a polymer, arranged to allow delivery of the agent to the target at controlled rates over a specified period (Lewis and Cowsar, 1977). The wide use of controlled-release fertilisers in agricultural sector had also facilitated research on this subject. The rapid emergence of controlled-release as an established scientific field is evidenced by the growing number of related works and publications appearing in the literature and symposia each year.

Controlled-release Products

The controlled-release products first appeared on the market in the early 1970s. Many of these products were introduced as pet flea collars and time release cold capsules. Since then, many other controlled-release products have been developed for consumers in agricultural and medical markets. Among the products in the agricultural chemicals sector, the slow-release fertilisers were the most widely used.

Most controlled-release fertilisers presently available are nitrogen carriers, while formulations involving other elements are also under evaluation. Aarnio *et al.* (1995) found that slow release ureaformaldehyde (UF) did not increase nitrification activity and it had a positive effect on microbial activity in soil. The use of the slow release non-leaching fertilisers has brought the Waasagaming golf course in Manitoba, Canada in line with the natural ecosystem habitat for small animals (Love, 1994). Kulyukin *et al.* (1993) found that application of encapsulated nitrogen and potassium slow release fertilisers before planting, produced a high tomato crop yield.

The crop could be sustained for up to 8 months, while preventing excessive nitrate accumulation and the need for top dressing.

A number of controlled-release systems and products for pesticides are currently in the market. Membrane moderated diffusion systems for home use such as Hercon Lure N Kill™, Fly Tape and Roach Tape® are laminated reservoir devices developed by Health Chem Corporation (Quisumbing *et al.*, 1976). The products were reported to be effective for at least three months. Another product is Shell No-Pest Strip® containing dichlorvos that dissolves in PVC matrix (Lewis and Cowsar, 1977). No-Foul® Rubber developed and marketed by B. F. Goodrich Company has proven successful as an antifouling coating effective for a period of up to 92 months (Ovalette and King, 1976).

In case of insecticides, the controlled-release chlorpyrifos (SuSCon Blue®) is currently used in Australia for controlling canegrubs (Allsopp *et al.*, 1995). Cokmus and Elciin in 1995 showed a high response of culex larvae to the encapsulated *Bacillus thuriangiensis* subsp. *israelensis* Bti. The containing spores and toxin crystals was encapsulated in an insolubilized carboxy methylcellulose (CMC)-aluminium matrix. The result suggested that the formulation could be employed effectively in the field.

Although there are herbicides prepared as controlled-release formulations such as thiobencarb (Soltan *et al.*, 1996), 2,4-D (Cardarelli, 1976; Young and Nelson, 1969) and phenylurea herbicides (Cotterill and Wilkin, 1996), controlled-release formulations of agricultural herbicides are still relatively few. Duncan and Seymour (1989) had formulated micro-encapsulated herbicide (Capsolene®) containing S-