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MODIFICATION OF ALGINATE CONTROLLED-RELEASE FORMULATIONS OF ALACHLOR AND DIURON WITH PECTIN: THEIR RELEASE KINETICS AND EFFICACY

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By

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Agricultural Science

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Faculty : Agriculture

Controlled-release formulation (CRF) of alachlor and diuron were prepared by a monolithic system using low methylester pectin and high methylester pectin as the polymers for the purpose of improving the initial release of active ingredient (a.i.) from the formulations. The release rates for both herbicides were evaluated by chemical assay and bioassay. Chemical assay using high performance liquid chromatography with ultra-violet detector showed the pectin-kaolin CRFs (P1K1, P2K1, P1K and P2K) release a.i. was faster compared with alginate:pectin-kaolin CRFs (AP1K1, AP2K1, AP1K and AP2K) and alginate-kaolin CRFs (AK1 and AK2), six hours after placement in water. The release reached a constant level at three, five and seven days after placement in water for pectin-kaolin, alginate:pectin-kaolin and alginate-kaolin CRFs, respectively.

The determination of release rate by bioassay technique was conducted in the glasshouse using *Cucumis sativus* and *Brassica juncea* seedlings as bioindicators for alachlor and diuron, respectively. At 3 days, after treatment (DAT), the CRF of alachlor (AP1K1, AP2K1, P1K1 and P2K1) showed a better performance in inhibiting shoot and root length of *C. sativus* compared to AK1. Similar result was observed for fresh weight of *C. sativus* at 15 DAT. The AP1K1, AP2K1, P1K1 and P2K1 also showed a similar performance with the conventional spray formulation of alachlor (CF1) at the initial treatments. These indicated that the presence of pectin in the CRF improved the initial release of alachlor. At 160, DAT, all the CRFs showed a better effect compared to CF1 indicating the prolonged activity of alachlor through the CRF. Similar results was observed for the CRFs of diuron in inhibiting germination of *B. juncea*. At 7 DAT, the pectin-koalin CRF (P1K and P2K) showed similar performance with the conventional spray formulation of diuron (CF) and significantly higher mortality was recorded from the CRFs of diuron compared to CF at 120 and 160 DAT.

The best composition of alginate:pectin CRFs based on the physical structure of the CRF granule, release rate and effect on the initial treatment was selected for the preparation of agricultural waste by-product (AWP) CRFs. Chemical assay showed that alginate:pectin-sawdust for both herbicides released more a.i. into distilled water compared to other formulations at 6 hours after placement. The release was recorded to reach a constant level 50 hours after placement in the water. The effectiveness of AWP and selected alginate/pectin-kaolin of CRFs on *Paspalum conjugatum* and *Diodia ocimifolia* was evaluated in the glasshouse. At 7 week after treatments (WAT), all the

CRFs of alachlor except P1K1 and P2K1 showed a lower germination of *P. conjugatum* compared to CF1. In contrast, only AK1, AP2K1, P1K1, P2K1 and ALSAW1 showed a lower germination of *D. ocimifolia* compared to CF1. The effectiveness of diuron CRFs on *P. conjugatum* showed a lower germination for all CRFs compared to CF except AK2, P1K, and AP1SAW. On *D. ocimifolia,* only AP1SAW, AP1PH and AP2PH showed a significantly lower germination compared to CF. In general, the alachlor alginate:pectin-koalin CRF of AP2K1 showed a better control on germination of both weeds.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains Pertanian

PENGUBAHSUAIAN TERHADAP ALGINAT FORMULASI RACUN LEPASAN TERKAWAL ALAKLOR DAN DIURON DENGAN PEKTIN: KINETIK PERLEPASAN DAN EFIKASI

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Formulasi racun lepasan terkawal (CRF) alachlor and diuron telah dihasilkan melalui satu sistem monolitik menggunakan pektin metilester rendah dan pektin metilester tinggi sebagai polimer dengan tujuan memperbaiki perlepasan awal bahan aktif (b.a.) dari formulasi. Kadar perlepasan bagi kedua-dua racun ini telah dinilai secara asai kimia dan bioasai. Asai kimia menggunakan kromatografi cecair bertekanan tinggi dengan pengesan UV telah menunjukkan CRF pektin:kaolin (P1K1, P2K1, P1K and P2K) melepaskan b.a. lebih cepat berbanding alginat:pektin-kaolin (AP1K1, AP2K1, AP1K and AP2K) dan alginat-kaolin (AK1 and AK2), enam jam selepas diletak dalam air. Perlepasan telah mencapai tahap malar pada tiga, lima dan tujuh hari selepas diletak dalam air masing-masing bagi CRF pektin-kaolin, alginat:pektin-kaolin dan alginat-kaolin.

Penentuan kadar perlepasan melalui teknik bioasai telah dijalankan di dalam rumah kaca menggunakan anak benih *Cucumis sativus* dan *Brassica juncea* sebagai penunjuk, masing-masing untuk alaklor dan diuron. Pada 3 hari selepas rawatan (DAT), CRF alaklor telah menunjukkan prestasi yang lebih baik bagi menghalang pemanjangan pucuk dan akar *C. sativus* berbanding AK1. Keputusan yang serupa telah diperhatikan ke atas berat basah *C. sativus* pada 15 DAT. Di awal rawatan AP1K1, AP2K1, P1K1 and P2K1 juga telah menunjukkan prestasi yang sama dengan formulasi lazim alaklor (CF1). Ini menunjukkan kehadiran pektin dalam CRF telah memperbaiki perlepasan awal alaklor. Pada 160 DAT, semua CRF telah menunjukkan prestasi yang serupa berbanding CF1, ini menunjukkan aktiviti CRF alaklor lebih berpanjangan. Keputusan yang serupa telah diperhatikan untuk CRF diuron dalam mengawal percambahan *B. juncea*. Pada 7 DAT, pektin-kaolin CRF (P1K dan P2K) telah menunjukkan prestasi setanding dengan formulasi lazim diuron (CF) dan keberertian kematian yang lebih tinggi telah direkodkan oleh CRF diuron berbanding CF pada 120 dan 160 DAT.

Komposisi yang terbaik dari CRF alginat:pektin berasaskan kepada struktur fisikal granul CRF, kadar perlepasan dan kesan ke atas rawatan awal telah dipilih untuk menyediakan CRF sisa buangan pertanian (AWP). Asai kimia telah menunjukkan alginat:pektin-habuk papan (SAW) untuk kedua-dua racun telah membebaskan lebih b.a. dalam air suling berbanding lain-lain formulasi pada 6 jam selepas diletakkan dalam air. Perlepasan telah direkodkan mencapai tahap malar 50 jam selepas diletakkan dalam air. Keberkesanan AWP dan CRF alginat/pektin-kaolin yang terpilih ke atas *P. conjugatum* dan *D. ocimifolia* telah dinilai di dalam rumah kaca. Pada 7 minggu selepas rawatan

(WAT) semua CRF alaklor melainkan P1K1 and P2K1 telah menunjukkan percambahan *P. conjugatum* yang lebih rendah berbanding CF1. Sebaliknya, hanya AK1, AP2K1, P1K1, P2K1 dan AP1SAW1 menunjukkan percambahan *D. ocimifolia* yang lebih rendah berbanding CF1. Manakala keberkesanan CRF diuron ke atas *P. conjugatum* juga telah menunjukkan percambahan yang lebih rendah untuk semua CRF berbanding CF melainkan AK2, P1K dan AP1SAW. Bagi *D. ocimifolia* hanya AP1SAW, AP1PH dan AP2PH yang telah menunjukkan percambahan yang lebih rendah berbanding CF. Secara umumnya CRF alginat:pektin-kaolin alachlor iaitu, AP2K1 telah menunjukkan kawalan percambahan yang lebih baik bagi kedua-dua jenis rumpai.

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I certify that an Examination Committee met on 13rd June 2003 to conduct the final examination of Sopiah Basari on her Master of Agricultural Science thesis entitled "Modification of alginate controlled-release formulations of alachlor and diuron with pectin: their release kinetics and efficacy" in accordance with Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any degree at UPM or other institutions.

(SOPIAH BASARI)

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CHAPTER 1

INTRODUCTION

The trends in pesticide consumption in some countries clearly indicate that pesticides are not only a critical input in pest management, mainly to increase crop production, but also for public health, recreation and forestry. One of the major types of pesticide used is herbicide. Since three decades ago, many experiments have been conducted on the development of sustained release of herbicides in order to reduce the loss through chemical and microbial processes in the soil. An effective approach to reduce these loses is through controlled-release technology. Flynn *et al.* (1994) showed that the controlled-release formulation reduced volatile loss of herbicide from 52% to 18% and phytotocixity on plant by 45% compared with EC formulation.

The principle of controlled-release technology was pioneered by the drug industry more than a century ago. The initial goal of producing controlled-release oral drug is to maintain effective level of drug in the body (Duncan *et al.* 1989). The first controlled-release herbicide was developed in 1969 when the ester of 2,4-D was formulated in natural rubber. Since then, various methods and polymers were developed for encapsulation of herbicides.

The controlled-release technology is also used to improve the performance and reduce the environmental impact of pesticide. These includes assurance of reliability of performance, lack of residues after termination of the effective release period, low cost of materials and production and also adaptability to wide range of farming techniques (Wilkin, 1978). The use of additives such as a small amount of high polymer molecules in formulations not only improves the physical properties of the formulations but also affects the rate of release of the active agent.

Studies by Coftman and Gentner (1980) have shown that trifluralin prepared by starch-encapsulated formulation persisted longer than the EC formulation when tested in the greenhouse and field condition. In 1995, Rajagopalan *et al.* used a technique of double encapsulation of carbofuran in starch urea formaldehyde (starch-UF) and they obtained a better performance than the EC formulation in paddy cultivated under flooded condition. Other polymers used include kraft lignin (Dellicolli, 1977; Chanse *et al.* 1987) and calcium alginate (Connick *et al.*1982; Hussain *et al.* 1992; Mardi, 1994) which is the most widely used biopolymer as encapsulation agent is calcium alginate.

Mazlan (1999) showed that the granule size affects the rate of release. Smaller granules released a.i. faster than bigger granules. Fillers also influenced the efficacy; between the three agriculture products that were used as a filler, the sawdust formulation gave a better control of *Paspalum conjugatum* and *Diodia ocimifolia* compared with the paddy husk and oil palm empty fruit bunch formulations.

Most of the previous works showed that the controlled-release formulation gave a good control of weed over a longer period of time, but the initial release of toxicant was slow. This led to a lower efficacy in weed control at the early stage (Mardi, 1994; Mazlan, 1999). Thus, the objectives of this research were :-

a). To study the effect on pectin as a substitute for alginate on the release rate of alginate/pectin-kaolin controlled-release formulation (CRF) of alachlor and diuron.

b). To evaluate and compare their release rates by bioassay.

c). To determine their effectiveness against *Diodia ocimifolia* and *Paspalum conjugatum.*

CHAPTER 2

REVIEW OF LITERATURE

Herbicide for crop protection

Herbicides began to make their appearance in the first half of the twentieth century. In 1897, it was discovered in France that a 2% solution of copper sulphate killed charlock (*Sinapsis alba*) in wheat without causing damage to the wheat. By early 1945, 2,4-D was marketed as 'weedone' for broadleaf control and dinoseb was marketed by Dow in the 50s as a contact herbicide for use prior to crop emergence. In the early 60s, chloramben was introduced as the first compound that gave good control against a range of major grasses and broad-leaf weeds. It was safe to the crop and consistent in its performance in the midwest of the USA (Lever, 1990).

Roberts (1982) used a mixed herbicide formulation to get the best control for weed control in a crop. The concept that an optimum weed management system employs multiple herbicides rather than a single herbicide. For example, combination of a triazine and acetanilide successfully controlled grasses and broadleaf weeds in of corn (Barrett, 1993). In 1986, Teng and Teh were also successfully developed a commercial mixture of glyphosate IPA + picloram known as MON-8010 for general weed control in rubber plantation. Other mixtures have been developed include butachlor + 2,4-D (IBE) for