ISSN : 1812-5379 (Print)
ISSN : 1812-5417 (Online)
http://ansijournals.com/ja

JOURNAL OF AGRONOMY

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Journal of Agronomy 6 (2): 370-373, 2007
ISSN 1812-5379

Controlled-Release Formulations of Butachlor and Oxadiazon-An Evaluation of Sorption/Desorption

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Abstract: Controlled-release herbicide formulations have significant role in slow release of herbicides under laboratory and field conditions. In the present study kaolin, clay and saw dust were used to sorb the herbicide butachlor to test the slow release formulations of herbicides and their kinetic retention behavior in water. Release of different formulations of butachlor and oxadiazon were also studied. Desorption of oxadiazon formulations OA1 showed higher release (93.98±0.34%) than OA2 (43.73±0.45%), butachlor formulations BH1 exhibited higher release (99.29±0.33%) than BH2 (59.45±0.30%) on 28th day. It was experimentally confirmed that clay and saw dust as a coating material have high adsorption rate (77.2%), found to increase the holding capacity of butachlor rather than kaolin and the release was very slow which may avoid herbicide loss by environmental degradation. Organoclays and saw dust may find application as better sorbents of herbicides than kaolin and this will be a promising formulation in the environmental and economic point of view.

Key words: Controlled release formulations, alginate-kaolin, saw dust, clay, butachlor, oxadiazon

INTRODUCTION

The adsorption and desorption on the soil play an important role in the effective functioning of pesticides particularly herbicides. As a result of adsorption, the concentration in the liquid phase is lowered reducing the amount of available herbicide, both for its beneficiary action and also for its degradation. In Controlled Release Formulations (CRFs) the herbicide is adsorbed onto inert materials like kaolin/sodium alginate beads. Such beads when sprayed on soil, reduce the losses by physico-chemical forces of dissolution, biotic factors and it will be an efficient, safer and selective means of dispensing herbicides with reduced environmental side effects (Scher, 1999). The composition of the formulations can also suitably be altered so that the release rate is regulated at a desired level. It gives the major advantage in rice farming system where the herbicides are broadcasted before transplantation of the seedlings from the nursery.

CRFs can reduce environmental pollution and other side effects associated with the use of agrochemicals (Akelah, 1996). The risk of ground water contamination resulting from rapid leaching of highly soluble pesticides can be minimized through the application of the pesticide adsorbed on a matrix or carrier, which limits the amount of pesticide immediately available for undesirable losses (Kalkhoff *et al.*, 1998; Celis *et al.*, 2002). El-Nahhal *et al.* (2001), prepared CRFs of herbicide with organoclays as sorbents and it prevent the herbicide from reaching deep soil layers and injuring perennial crops grown on sandy soils under sprinklers and deep irrigation. All CRFs have several advantages over conventional formulations: slow, extended, constant release of active ingredient, reduced phytotoxicity and better targeting, etc. They provide economic savings in the cost of active ingredient because less active material is needed for maintaining effective biological activity.

Adsorption will vary upon the properties of soil such as clay content, organic matter content, Ca^{2+} ion exchange capacity and surface area (Burns *et al.*, 2006). The mobility of herbicides in soil is influenced by soil organic matter and pH (Basham *et al.*, 1987). Higher organic content of the soil causes the increased adsorption of herbicide and this supports the fact that herbicidal activity decreases with increase in organic soil content (Ben-Hur *et al.*, 2003). And it may occur as a result of transformation of the pesticide in liquid phase (Bosten and Van Der Pas, 1988).

We have studied the release of three herbicides: oxadiazon and butachlor into water by CRFs with the modified formulations by substituting the mixture of clay

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and saw dust for kaolin. The specific aim of this study was to determine the desorption rate of CRFs of herbicides using alginate-kaolin encapsulation and to compare the sorption/desorption process of butachlor by microencapsulation of CRFs with different sorbent materials: alginate-kaolin and low cost materials like saw dust-clay.

MATERIALS AND METHODS

The study was conducted at Department of Molecular Microbiology, School of Biotechnology, Madurai Kamaraj University, Madurai, India during February 2006 to May 2006.

CRFs of butachlor formulations BH1 and BH2 (N-(butoxymethyl)-2-chloro-N-(2,6-diethylphenyl)-ethanamide) and oxadiazon formulations OA1 and OA2 (3-(2,4-dichloro-5-propan-2-yloxy-phenyl)-5-tert-butyl-1,3,4-oxadiazol-2-one) were provided by (International Atomic Energy Agency (IAEA), Vienna, Austria) and their composition is given in Table 1. ^{14}C-labelled butachlor (43.475 MBq g^{-1}) with 99% purity was also supplied by IAEA. All the experiments were performed in three replications.

Preparation of CRFs for ^{14}C-Butachlor with kaolin: Three replicates of 250 mg sodium alginate were stirred in 18.75 mL of double distilled water until alginate was completely dissolved without air bubbles. 2.5 g kaolin was added in small batches to the mixture and stirred to get homogenous slurry. Unlabelled butachlor (500 mg) and 10 μg (89.543 Bq g^{-1}) of ^{14}C labelled butachlor was dissolved in 2 mL acetone, added to the slurry, mixed well for 15 min and added dropwise to 37.5 mL of 0.25 M calcium chloride solution. Resultant beads were kept in calcium chloride solution for 30 min, filtered, washed twice in the double distilled water and dried (Gan *et al*., 1994).

Preparation of CRFs of ^{14}C-Butachlor with clay and saw dust: CRFs of ^{14}C-Butachlor with clay-saw dust was prepared by adopting the procedure as mentioned in ^{14}C-Butachlor-kaolin formulation and the addition of kaolin was replaced by clay (2.5 g) with saw dust (2.5 g). The retention/sorption of added herbicides in the formulation was estimated by counting 1 mL of calcium chloride solution and double distilled water wash (Gan *et al*., 1994).

Table 1: Herbicide formulations used

Formulations	Composition (%)
OA1	Oxadiazon (4), (PVA) (4), POEG (8), Corncob (84)
OA2	Oxadiazon (4), PVA (8), POEG (4) Corncob (84)
BH1	Butachlor (6.5), Alginate
BH2	Butachlor (8.1), Alginate, Kaolin

Evaluation of controlled release of ^{14}C-labelled butachlor, OA1, OA2, BH1 and BH2 in water: The formulations prepared with ^{14}C-labelled butachlor (kaolin) and ^{14}C-labelled butachlor (clay soil-saw dust) were added to 1 L distilled water in flasks separately, kept at 28±2°C in dark to prevent photo degradation. Aliquot of 4 mL was withdrawn on 2, 5, 8, 25, 36 and 48 h and 1, 3, 5, 7, 9, 14, 21, 28 and 30 days from formulation with ^{14}C-labelled butachlor (kaolin), OA1 and OA2. Formulation with clay soil and saw dust were withdrawn at 1, 2, 3, 4 and 8 weeks. From the above aliquot, 1 mL of the sample was added to 6 mL of liquid scintillation cocktail (Insta-Gel) (Gilman *et al*., 1998) in a sterile glass vial and analyzed for the released radioactivity in Packard Tricarb 4000 series scintillation counter with Insta-Gel (Packard) as scintillator. Quench corrections were determined by external standard calibration. Before withdrawing the aliquots, the flasks were gently stirred and the contents were allowed to settle for 30 min. Release of herbicide formulations; oxadiazone (OA1 and OA2) and butachlor (BH1 and BH2) were analyzed in triplicates. The above results were confirmed by HPLC, the extraction was done using liquid-liquid partitioning technique using benzene.

RESULTS

Release of OA1, OA2, BH1 and BH2: The release/desorption experiment exhibited the oxadiazon (OA1 and OA2) and butachlor (BH1 and BH2) formulations were started releasing oxadiazon and butachlor from the second hour (OA1, OA2, BH1 and BH2 into 11.65, 4.38, 3.07 and 2.04%, respectively) and showed gradually increased desorption. In the fourth week, the faster releasing formulations OA1 and BH1 have released 93.98 and 99.29%, respectively when compared to the other two formulations OA2 and BH2 (the slower releasing formulation), 43.73 and 59.45%, respectively (Table 2).

Table 2: Desorption of active ingredient of Oxadiazon and Butachlor from different formulations

	Release of oxadiazon (%)		Release of butachlor (%)	
	OA1	OA2	BH1	BH2
Time (days)				
1	30.00±0.56	12.40±0.42	12.05±0.41	9.50±0.36
7	72.80±0.53	25.00±0.53	50.00±0.37	27.50±0.47
14	70.40±0.42	24.10±0.58	57.50±0.51	32.50±0.48
21	86.00±0.37	36.80±0.43	72.80±0.40	42.60±0.35
28	93.98±0.34	43.73±0.45	99.29±0.33	59.45±0.30
Time (h)				
2	11.65±0.57	4.38±0.62	3.07±0.58	2.04±0.51
5	20.00±0.49	8.00±0.57	5.08±0.52	4.00±0.57
8	21.00±0.56	9.00±0.61	9.00±0.56	6.00±0.49
25	29.00±0.51	11.00±0.57	13.00±0.42	8.00±0.42
36	38.00±0.46	15.00±0.48	16.00±0.39	9.00±0.58

All the samples were analyzed in triplicates. Values are the means of three replications±SD

Table 3: ^{14}C-Butachlor release in water from sorbent Kaolin and sodium alginate

No. of days	Release of Butachlor* (%)	Release of Butachlor** (%)
1	7.6±0.53	26±0.62
3	62.5±0.67	26±0.68
7	98.0±0.58	30±0.58
9	-	35±0.69
11	-	38±0.42
20	-	46±0.57
25	-	42±0.46
30	-	40±0.56

The analysis was performed in triplicates and represented as the mean value of three replications±SD; *Denote the CRF preparation not kept for aging and **Denote the CRF samples kept for aging for 6 days

Table 4: Release of ^{14}C-Butachlor with clay soil and saw dust after aging

Time (h)	Release of Butachlor* (%)
2	32.8±0.60
4	31.8±0.69
8	36.1±0.57
12	39.2±0.51
24	43.6±0.63
36	43.0±0.69
44	42.0±0.52
60	44.3±0.43
72	44.5±0.49

*Denote the % release of butachlor kept for aging (6 days). Samples were analyzed in triplicates. Values are the means of three replications±SD

Release of ^{14}C-Butachlor with kaolin: The formulation prepared using sodium alginate and kaolin only 50% of the added ^{14}C-butachlor was adsorbed. The release/desorption studies from these formulations, showed release of 7.6% butachlor on the first day, 62.5% on the third day and 98% on the seventh day. According to Bosten and Van Der Pas (1988), the adsorption equilibrium may be either in terms of hours or days. Thus the slurry of alginate-kaolin and butachlor was aged for 6 days at room temperature. On the 7th day the slurry was stirred, filtered, dried and the release/desorption experiments were observed. The formulation started releasing the butachlor from the first day itself (26.17%) and it gradually increased. The maximum amount was released on the 20th day (46%). On 25th and 30th day, it showed a slight decreasing trend. On the 32nd day, residual butachlor in the formulation was 32.8%. According to Friedman (1997) the process of desorption is generally slower than adsorption in all CRFs. The above finding well correlates with present study. Formulation which was not kept for aging released maximum amount of butachlor on 7th day (98%). After increasing the time for adsorption by aging for 6 days, the formulation retained 80.24% of butachlor added. Then, the release/desorption also takes place slowly and released maximum on the 20th day (Table 3).

Release of ^{14}C-Butachlor with Clay soil and saw dust: CRF prepared with saw dust and clay (not aged) showed 90% of butachlor adsorption in the beads. The process was prolonged for 6 days (aged) to increase the time of adsorption. In aged formulations, nearly 91.58% of added butachlor was adsorbed to the beads. The formulation started releasing from the second hour itself (32.8±0.6%). After the second hour, it was found that desorption was very slow with more or less constant and steady up to 72 h (Table 4). This type of formulations is useful for the agricultural practices.

DISCUSSION

The different physical properties like smaller particle size, greater surface area, interactions between dissolution media, polymer and herbicide are the primary factors in release of herbicides (Sopeña *et al*., 2005) and in the formulation OA1, PVA (poly vinyl acetate 4%) was more porous than OA2 (PVA 8%). This porosity may be the important factor in desorption of oxadiazon which is released into water faster than the formulation OA2.

The butachlor formulation BH1 was prepared with butachlor alginate whereas the formulation BH2 (slow release) was prepared with butachlor, alginate and kaolin. Kaolin is a soil product, to which butachlor will strongly adsorb and desorption will be slow. In the formulation BH1, the added herbicide butachlor may adsorbed onto alginate, which may be a weak adsorbent and exhibited faster release of adsorbed butachlor than BH2. The synthetic cationic surfactants, organic polymers and natural plant materials like lignin and starch materials have been found to have the adsorbing property for the slow release formulations of pesticides thus causes the efficient release to the crop based cultivation system (Gish *et al*., 1994; Johnson and Pepperman, 1995).

The commercially available clay-based slow release formulation of fluridone, Sonar SRP with 5% active ingredient, was reported to have a release rate of 10 to 16 days (Mossler *et al*., 1993) and in a static pond; it reached a peak concentration 15 days after treatment (Netherland *et al*., 1998) and in the present study, the butachlor with clay and saw dust sorbent gave the release rate of 47.1% even when analyzed on the second week and this type of formulations are good in periodical release. Organic clays are used in the powdered and granular formulations of pesticides for a long time release in CRFs (Gerstl *et al*., 1998; Cox *et al*., 2000). The adsorption of butachlor increased with increased clay content in soil. Thus the retention was high up to 77.2% and it was observed that the clay saw dust sorbent combination exhibited significant slow release of butachlor.

From this study, it is concluded that there is a need to have a study on the interaction of herbicides with sorbent materials like sawdust and clay. The increased use of agrochemicals to enhance the crop yield will lead to many adverse side effects like human and animal health problem and environmental pollution. If such chemicals are released in to the environment with the low cost slow release formulations as described in this study like saw dust and clay, it will reduce the cultivation cost and provide prolonged supply of pesticides to kill the target organisms.

ACKNOWLEDGMENT

We are thankful to International Atomic Energy Agency, Vienna, Austria for supplying CRFs and financial assistance.

REFERENCES

Akelah, A., 1996. Novel utilizations of conventional agrochemicals by controlled release formulations. Mater. Sci. Eng. C., 4: 83-98.

Basham, G.W., T.L. Lavy, L.R. Oliver and H.D. Scott, 1987. Imazaquin persistence and mobility in three Arkansas soils. Weed Sci., 35: 576-582.

Ben-Hur, M., J. Letey, W.J. Farmer, C.F. Williams and S.D. Nelson, 2003. Soluble and solid organic matter effects on atrazine adsorption in cultivated soils. Soil Sci. Soc. Am. J., 67: 1140-1146.

Bosten, J.J.T.I. and L.J.T. Van Der Pas, 1988. Modeling sorption/desorption kinetics of pesticides in a soil suspension. Soil Sci., 4: 221-231.

Burns, I.G., M.H.B. Hayes and M. Stacey, 2006. Studies of the adsorption of paraquat on soluble humic fractions by gel filtration and ultrafiltration techniques. Pestic. Sci., 4: 629-641.

Celis, R., M.C. Hermosin, M.J. Carrizosa and J. Cornejo, 2002. Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone. J. Agric. Food Chem., 50: 2324-2330.

Cox, L., R. Celis, M.C. Hermosin and J. Cornejo, 2000. Natural soil colloids to retard simazine and 2,4-D leaching in soil. J. Agric. Food Chem., 48: 93-99.

El-Nahhal, Y., T. Undabeytia, T. Polubesova, Y. Mishael, S. Nir and B. Rubin, 2001. Organo-clay formulations of pesticides: Reduced leaching and photodegradation. Applied Clay Sci., 18: 309-326.

Friedman, S.P., 1997. Agrochemical controlled-release and transport in the soil profile: I. Model formulation and sensitivity analysis for bare soil under field conditions. Eur. J. Soil Sci., 48: 523-533.

Gan, J., M. Hussain and N.M. Rathor, 1994. Behaviour of an alginate-kaolin based controlled-release formulation of the herbicide thiobencarb in simulated ecosystems. Pestic. Sci., 42: 265-272.

Gerstl, Z., A. Nasser and A. Mingelgrin, 1998. Controlled release of pesticides into water from clay-polymer formulations. J. Agric. Food Chem., 46: 3803-3809.

Gilman, S.D., S.J. Gee and B.D. Hammock, 1998. Analytical performance of accelerator mass spectrometry and liquid scintillation counting for detection of ^{14}C-labeled atrazine metabolites in human urine. Anal. Chem., 70: 3463-3469.

Gish, T.G., A. Shirmohammadi and B.J. Wienhold, 1994. Fieldscale mobility and persistence of commercial and starch-encapsulated atrazine and alachlor. J. Environ. Qual., 23: 355-359.

Johnson, M. and A.B. Pepperman, 1995. Metribuzin mobility from alginate-encapsulated controlled release formulations. J. Agric. Food Chem., 43: 241-246.

Kalkhoff, S.J., D.W. Kolpin, E.M. Thurman, I. Ferrer and D. Barcelo, 1998. Degradation of chloroacetanilide herbicides: The prevalence of sulfonic and oxanilic acid metabolites in Iowa groundwaters and surface waters. Environ. Sci. Technol., 32: 1738-1740.

Mossler, M.A., D.G. Shilling, K.E. Milgram and W.T. Haller, 1993. Interaction of formulation and soil components on the aqueous concentration of fluridone. J. Aquat. Plant Manage., 31: 257-260.

Netherland, M.D., D. Sisneros and A.M. Fox, 1998. Field Evaluation of low-dose metering and polymer endothall applications and comparison of fluridone degradation from liquid and slow-release pellet applications. Tech. Rep., 1: 66.

Scher, H.B., 1999. Controlled-Release Delivery Systems for Pesticides. Marcel Dekker Inc: New York.

Sopeña, F., A. Cabrera, C. Maqueda and E. Morillo, 2005. Controlled release of the herbicide norflurazon into water from ethylcellulose formulations. J. Agric. Food Chem., 53: 3540-3547.