Controlled release agrochemicals formulations: A review

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This study reviews controlled release formulation (CRF) of agrochemicals (fertilizers, pesticides, herbicides, plant growth regulators etc.). Synthetic as well as naturally occurring polymers have been used for preparation of these formulations. Dual applications of polymer supported herbicides have also been attempted. This strategy would open new areas for prevailing registered pesticides in India. Scope of CRF in controlling other pests like mosquito is also visualised.

Keywords: Agrochemicals, Controlled release formulation (CRF), Pesticides, Polymers

Introduction

Applied conventional agrochemicals (90%) never reach their objective to produce desired biological response at the precise time and in precise quantities required, due to nonspecific and periodic application of active agents. Both factors, besides increasing treatment cost, produce undesirable side effects to plant or environment\(^1\). Widespread application of different polymeric materials as reactive molecules is based on potential advantages of specifically active functional groups and characteristic properties of polymeric molecules\(^2,3\). Conventional application of agrochemicals results in groundwater contamination\(^4\). Also, over application and point source contamination increase pollution potential\(^5\). Replacement of conventional agrochemical formulations by controlled-release systems not only helps to avoid treatment with excess amounts of active substances, but also offers, besides ecologic and economic advantages, the most suitable technical solution in special fields of application (in aquatic weed control and pest management in paddy fields). Controlled-release formulations (CRF) are used to maintain effective local concentration of active ingredients in the soil and to reduce runoff\(^6\). Conventional application of agrochemicals provides an initial concentration far in excess than required and cause toxicity problems for organisms\(^7\) and also produces undesirable side effects in the environment.

CRF has following advantages\(^8,9\): 1) Activity prolongation by providing continuously low amount of pesticide, a level sufficient to perform its function over a long period; 2) Reduced number of applications by achieving a long period of activity duration through a single application; 3) Cost reduction by eliminating time and cost of repeated and over applications; 4) Environment pollution reduction by eliminating the need for widespread distribution of a large amount of pesticide one time, thereby reducing undesirable side effects of agrochemical losses by evaporation and degradation or leaching by rain into the soil or waterways; 5) Extending activity duration of less persistent pesticide, which is unstable under an aquatic environment; 6) CRF converts technical pesticide liquid into solid formulation, resulting in easily transported material with reduction of flammability; and 7) Mammalian and phytotoxicity reduction by lowering high mobility of pesticide in soil and hence reducing their residue in food chain. High cost involved in manufacturing of these formulations, excessive amount of polymer used and polymeric herbicide is the fate of polymer matrix\(^10-12\).

This review presents CRF of agrochemicals, particularly pesticides.

Controlled Release Formulations (CRF) Technology

CRF technology is based on interaction of pesticides with polymers. Developed methods are classified as per
the material or technology used for their preparation as follows:

**Diffusion of Pesticide in Polymeric Medium**

This technology includes two types of products: i) Monolithic system, where pesticides are dispersed uniformly in polymeric or elastomeric matrices; and (ii) Reservoir system, where pesticides are covered by membranes, laminate, capsule, coating, liposome etc.

**Polymeric Pesticides**

Pesticide is bound via covalent or ionic bonds to polymers or pesticide formulation may also be obtained by binding pesticide to monomers, followed by polymerization. Pesticide is released from polymeric matrix by hydrolysis of polymer-pesticide bond in the environment. Pesticide that contains very reactive functional groups (carboxyl, hydroxyl, and amino etc.) can react with monomers or polymers directly. In case pesticides do not have any functional groups, some bridging agents are needed in order to bind pesticide to monomers or polymers.

By this method various kind of pesticides are bound to natural polymers (kraft, lignin, and bark and saw dust) as follows: i) Erosion of Polymers – Pesticide is released by chemical or biological erosion of polymers from monolithic or reservoir system; ii) Porous Materials – This technique, where pesticide is retained in capillary channels (hollow fibres, porous plastic, and foam and so on), is used only for insect pheromones; iii) Adsorptive Carriers – Montmorillonite clays and attapulgite clays have adsorptive ability for various compounds including pesticides. The formulation thus obtained is released under controlled conditions and longer residual activity is expected. Activated charcoal may also be used for this purpose; iv) Propesticide – A modified molecule release active pesticide under certain conditions. One of the examples of propesticide for controlled release is pyrazolate; and v) Osmotic Pump – Pesticide is covered by semipermeable membrane with small holes.

**Chemical and Physical Methods of Controlled Release Agrochemical Formulations**

**Chemical Bonding of Pesticide to Polymer Matrix**

One of the basic methods to prepare CRFs of pesticides is via synthesis of polymer with pesticides as pendant substituent. Generally, there are two ways for preparation of polymers chemically bonded with pesticides: i) pesticide reacts with polymerizable monomer to give macromolecular combination; and ii) preformed synthetic or natural polymers are chemically modified with herbicide or herbicide derivatives.

**Polymerization of Herbicide-Containing Monomers**

Polymerization of herbicide-containing monomers depends on functional groups of both pesticide as well as monomer. Polymerization of herbicide containing monomers requires high monomer purity in order to obtain reasonable molecular weight. McCormick et al. synthesized a controlled-release system by polymerization of vinyl ester of 2, 4-dichlorophenoxy acetic acid (2, 4-D). Neogi & Allan prepared polymerizable monomers containing 2-methyl-4-chlorophenoxyacet acid and pentachlorophenol. Copolymer of monomer containing 2-methyl-4-chlorophenoxy acetic acid with acrylic acid (AA) was found biologically active.

Various controlled-release pesticide-polymer formulations have been developed. Harris’s group synthesized vinyl 2, 4-dichlorophenoxyacet and vinyl 2-(2, 4, 5-trichlorophenoxy) propionate by transvinylation. 2-Acryloxyethyl ester of 2, 4-D was copolymerized with triethylamine methacrylimide. Linear polymeric pesticides containing a pentachlorophenol moiety were synthesized by radical polymerization of vinyl monomers containing pentachlorophenol pesticide via ester linkage unit. Release of pentachlorophenol from these systems was reported to be mainly dependent on degree of hydrophilicity and temperature. Other systems were synthesized from vinyl monomers by introducing an oxyethylene moiety via ester group as a space between pentachlorophenol and vinyl moieties. These systems containing pentachlorophenol pesticide were polymerized under free-radical conditions and cross-linked using different ratios of divinyl benzene. Acryloyl chloride monomer carrier or its methyl derivative was reported to be useful in controlled release of niclosamide molluscicide. Polymers containing niclosamide were obtained either by homopolymerization or copolymerization of monomer with styrene or oligo-(oxyethylene) vinyl monomers in different molar ratios. Synthesis of N,N-diacryloyl metribuzin (DAMB), and herbicide-containing monomer was co-polymerized with acrylamide (AM) and AA. Co-polymerization of monomer in aqueous buffer systems indicated that hydrolysis of labial bond to release metribuzin was slow.
McCormick et al.\textsuperscript{35,36} synthesized and characterized co-polymers with pendent esters of plant growth regulators. Hydrolytic release behaviour\textsuperscript{36} for above formulations shows that it is dependent on nature of monomer structure and its composition. Another polymeric herbicide formulation was prepared using oligo-(oxyethylene) methacrylates loaded with either 2, 4-D or MCPA (2-methyl-4-chlorophenoxyacetic acid). Herbicide-containing monomer was homopolymerized or copolymerized with AM and other hydrophilic co-monomers such as 4-vinylpyridine\textsuperscript{37}.

CRF systems are of special interest because of their dual function in utilization as herbicide and fertilizers. Dual applications of polymer-supported herbicides are based on a combination of herbicide-fertilizer, in which polymer contains elements like nitrogen or phosphorus to act as a fertilizer in the soil after polymer degradation. Polymeric herbicides were synthesized by condensation of tartrate monomer with a series of diamines (ethylenediamine, triethylenetetramine, tetraethylenediamine, diethylenetriamine, triethylenetetramine). Akelah et al.\textsuperscript{12} prepared CRF based on polyureas and poly Schiff bases. These systems were synthesized by polymerization of monomer either with hexamethylenedisocyanate to yield polyurea or with terephthaldehyde to yield poly (Schiff bases). Akelah et al.\textsuperscript{38} also reported CRF from monomeric herbicides of diethanol amine using 2, 4-D or 2-methyl-4-chlorophenoxy acetic acid (DCPA). Use of natural and acid-treated bentonite\textsuperscript{39} as modifying agents for CRF development (sodium alginate-atrazine-water) reduces release rate of herbicide as compared with technical atrazine and with alginate formulation without modifying agents; and iii) highest decrease in release rate corresponds to the formulations prepared with activated carbon. Moreover, diffusion causes release of chloridazon and metribuzin from various alginate-based CRFs into water and in this diffusion sorption capacity of modifying agents for herbicides is the most influential factor\textsuperscript{42-47}. Gressel et al.\textsuperscript{48} successfully used imidazolinone resistant maize seed dresses with imazapyr to control parasitic weed striga. A series of slow release formulations were synthesized based on binding imazapyr to high capacity anion exchangers and using them to coat maize seed.

Chemical Modifications of Preformed Polymers with Pesticide or Pesticide Derivatives

Combination of pesticides with natural and synthetic polymers are comprehensively described\textsuperscript{49,50}. Similar systems were synthesized\textsuperscript{19} using 2, 4-D herbicide. Schacht et al.\textsuperscript{51} synthesised cyclic six member acetyl ring by reacting 2, 4-dichlorobenzaldehyde with PVA. Hartman & Wemann\textsuperscript{52,53} synthesized polymeric herbicides from modification of poly (acrylic acid). Wilkins & Blackmore\textsuperscript{54} modified kraft lignin with propachlor to produce polymeric, in which availability of active agent was extended to more than 9 weeks. Similar systems were prepared by Cho et al.\textsuperscript{55} using rice husk lignin and 2, 4-D. McCormick et al.\textsuperscript{56-58} reported a number of modifications of naturally occurring polymers with herbicides, and also reported a series of polymeric herbicides by modifying metribuzin with diisocyanate, which were further modified with PVA. Release studies from these systems using bioassay indicated phytotoxicity for Sida spinosa L.\textsuperscript{59}. A series of preformed polymers modified with pesticides has been reported\textsuperscript{2}. 2, 4-D or its salt was modified with either sawdust\textsuperscript{60,61}, bark\textsuperscript{62}, or pine kraft lignin\textsuperscript{63}. Ikladious & Messiha\textsuperscript{64} reported controlled release from an antifouling system based on treatment of copolymer of maleic anhydride and methylmethacrylate with tributyltin oxide. Chitin was used as a carrier for herbicide metribuzin\textsuperscript{65}, and system showed slow release when polymer was directly attached to metribuzin. Polyphosphazene\textsuperscript{66} containing 2, 4-D was of great interest because of its biodegradability with nitrogen and phosphorus-containing products in addition to active ingredients. Degradation products were found to be very useful as fertilizers.
Polymeric molluscicides were prepared by chemical modifications of preformed cross-linked polyacrylic acid (Amberlite resin IRC-50) or by modification of anion exchange resins Amberlite IRA-401 and IRA-400. Niclosamide from polymers indicated that release rates were strongly dependent on the nature of hydrolyzing medium and type of binding group, as well as degree of cross-linking. Two CRFs containing copper sulphate as a molluscicide loaded onto natural clays as binding agent have been reported. Release of copper ions in water follow a zero-order release kinetics with a theoretical lifetime of 270-350 days. Lignin was used as a carrier for 2,4-D, chlormeben, metribuzin, alachlor and diuron.

Mair et al. reported CRFs of pentachlorophenol using cellulose as a carrier. Chiellini & Akelah synthesized polymeric herbicides containing 2,4-D and MCPA by modification of oligoethyleneoxylated styrene/divinyl benzene (DVB) resins. Other systems were synthesized using various either linear or cross-linked poly [oligo (oxyethylene) methacrylate]s as main polymer. From release kinetics it was concluded that release profiles cannot be easily correlated with structural parameters (degree of cross-linking and distance of herbicide from polymer backbone). Cross-linked polysaccharides containing covalently bound 2,4-D were prepared by reacting alkaline water solutions of semisynthetic polymers (hydroxyethyl cellulose and dextrans) with epichlorohydrine in toluene, using an epichlorohydrin/glucose unit. 1-Naphthyl acetic acid (NAA), as a plant growth regulator, was synthesized using poly [oxytartaroyloxy poly (oxyethylene)]s [PTEGs] to give polymeric plant growth regulators. No release studies of these systems are reported.

Controlled-release Bayluscide systems were prepared by chemical reactions of commercial chloromethyl styrene (2% DVB) and Amberlite IR-120 (8% DVB) with Bayluscide. Resulting polymeric molluscicidés contain Bayluscide active group attached via covalent bond or through physical interaction with diethanol amine group of modified polymers. Release rates of niclosamide were found strongly dependent on medium pH and structure of composition of polymers. Kenway et al. prepared CRFs based on cross-linked polyacrylamide derivatives. Acrylamide gel derivatives were prepared by transamidation of cross-linked polymers with various diamines of different structures (ethylenediamine, hydrazine hydrate, jeffamine 148, bis-(3-aminopropyl)-polytetrahydrofuran 750, and bis-(3-aminopropyl)-polytetrahydrofuran 1100). Transamidated polyacrylamide gels were reacted with 2, 4-dichlorophenoxy acetyl chloride to produce polyacrylamide derivatives containing 2, 4-D.

Kulkarni et al. reported experimental results on successful encapsulation of a natural liquid pesticide ‘Neem’ seed oil or NSO, using sodium alginate (Na-Alg) as a polymer. SEM photographs indicate a spherical and smooth surface of the beads. Particle size was found to be independent of increasing exposure time to cross linking agent or on increasing percentages of loading of active ingredient. Higher release rates for NSO were observed for higher loading of NSO. An increase in degree of cross linking of precipitated Na-Alg polymer resulted in a significant decrease of NSO release from beads. Novel polymeric sodium alginate (Na-Alg) interpenetrating network (IPN) beads were prepared by cross linking Na-Alg blend with gelatine or egg albumin with glutaraldehyde as a cross linking agent. These beads were used for controlled release of chlorpyrifos. IPN polymeric beads of poly (vinyl alcohol) - gráfmed-acrylamide with Na-Alg have been prepared by cross linking with glutaraldehyde. Cypermethrin, a widely used pesticide, was loaded with 80% efficiency in these hydro gel beads. Diffusion of pesticides through polymeric beads decreases with increasing cross linking as well as increasing cypermethrin loading.

Clay minerals have been used as an inert material for development of CRFs of pesticides because of their larger specific surface area and considerable ion-exchange capacity, which attribute to their ability to absorb/desorbs pesticides. Besides controlling release of pesticides from CRF, clay minerals also help in supplying nutrients towards plants. Modification of alginate with kaolin and bentonite was found to reduce the release rate of pesticides from formulations. Singh et al. developed starch-alginate beads for controlled release of pesticides and release has been observed to increase with increase in starch concentration. Release of active was found to be dependent on percentage of Kaolin and bentonite in starch-alginate based bead formulation. Release of pesticides from these beads occurred in a controlled manner, a primary requisite for use of agrochemicals to control environment system and health hazards. Sanli & Isiklan successfully encapsulated carbaryl in alginate polymer. Alginate beads appear to be a good product for CRF for agrochemical formulation applications to improve pesticide stability and to reduce risk both to people who handle the product and to ground.
water. Pesticides (isoproturon, imidacloprid and cyromazine) were incorporated in lignin based formulations to obtain controlled release (CR) properties\textsuperscript{96}. Time taken analysis for 50% of active ingredient to be released into water (T\textsubscript{50}), showed that release rate were much higher in cyromazine CR formulation than in isoproturon. However, imidacloprid showed an intermediate release rate. Bajpai et al\textsuperscript{107} prepared biopolymer microsphere of sodium alginate and starch by employing calcium chloride as a cross linker. Prepared microsphere was loaded with an insecticide chlorpyrifos and microsphere was characterized by FTIR and SEM analysis. The result was further analyzed by Ficks power law equation\textsuperscript{97}. Singh et al\textsuperscript{98} prepared neem leaf powder and alginate based beads by using calcium chloride as cross linker. Maximum (78 ± 2.89%) swelling was found in beads prepared with NLP (1.5%), alginate (2.5%) and 0.1 M cross linker solution.

**Physical Combination of Pesticides with Polymers**

CRF systems based on stabilized natural rubber masterbatch were reported for 2,4-dichlorophenoxy acid butoxyethanol\textsuperscript{99}. Schacht et al\textsuperscript{100} reported systems based on suspending dichlorobenil into urea-formaldehyde prepolymer. These formulations were found to enhance herbicidal activity towards *Sagittaria pygmaea*, bull rush, and barnyard grass.

Choudary et al\textsuperscript{101} reported a novel technique for CR of pesticides based on encapsulation of pesticides via complexation with metals in interlamellars of montmorillonite. Intercalated pesticides were released in small amounts over a period of 7 to 8 weeks. Pesticides diazinon, trifluralin, and alachlor were successfully encapsulated into temperature-responsive interlamellar microcapsules\textsuperscript{102}. Prasad & Kalyanasundaram\textsuperscript{103} reported a CRF of mosquito larvicide fenthion as monolithic slabs by insolubilizing sodium carboxymethyl cellulose by ionotropic cross-linking with ferric chloride under ambient conditions of temperature and pH. Another system\textsuperscript{104} for herbicide Dicamba (DA) based on polymeric microspheres was produced from ethyl cellulose, polyarylsulfone, or a combination of the two. Release rate of DA from ethyl cellulose microspheres could be controlled using different viscosity grades, molecular weights of ethyl cellulose; higher the viscosity, lower the DA release rate. Metribuzin herbicide\textsuperscript{105-107} formulated with an alginate-clay system showed that standard composition of formulation, which can act like in controlled release product, is with formulation of: alginate, 1; metribuzin, 1; clay, 10; and water, 88%. Johnson & Pepperman\textsuperscript{108,109} reported two CRFs of atrazin based on Na-Alg (1%), kaolin, and Tween 20 (0.5%). First formulation was prepared with linseed oil (4%), and second formulation was without oil. Leaching potential of atrazin decreased with the use CRF; also, CRF increased amount of atrazin retained on soil surface horizon (58-93%) as compared with technical grade and commercial liquid treatments. Singh et al\textsuperscript{110} explained release of pesticide from CRFs is best strategy to reduce agro-environmental pollution. They synthesized pesticide delivery devices based on neem leaf powder, kaolin and bentonite. Incorporation of clays in beads was found to control release of thiram from formulations.

**Conclusions**

CRFs have various advantages such as labour-saving, safety for workers, smaller dosage, fewer applications and less environmental impact. Agrochemical-based CRFs are highly efficient in sustaining release of biological sense. A significant hurdle in promoting this technology is the high cost of these formulations developed but use of cheaper natural polymer waste materials (sawdust, paper, starch, rice husk, lignin, and pine Kraft lignin) seems to be a viable way to provide loading of active species. Other possible trends to reduce cost are to increase weight efficiency by increasing content of active ingredients and to use polymer itself in a positive role rather than as an inert vehicle. One of the possibilities of making formulations economically viable is to make polymer backbone having a dual function as a fertilizer and as a carrier for the active agent. Another way is to use hydro gels as a carrier, which at the same time, may play a role in water conservation.

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