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Review on Biopolymer Based Agrochemicals Formulations

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ABSTRACT

Polymers have been widely used in agriculture for many diversified applications including the area of controlled release (CR) technology for pesticides and other active ingredients (AI). The release studies involving agrochemicals can predict their delivery during application and thus make a significant contribution to design CR formulations and avoiding subsequent environmental hazards. The present article reviews the state of the art of macromolecular matrices which have been used as carriers in controlled release of variety of agricultural active agents. The article specifically focus on various aspects of controlled release technology in agricultural systems including various fabrication methods of controlled release formulations, advantages and mechanisms of controlled release processes, agrochemicals and their fate in agricultural fields, biodegradable polymers in agriculture.

Keywords: *Controlled Release, Agrochemicals, Biodegradable polymers, Hazardous Effect*

I. INTRODUCTION

The emergence of green revolution has resulted in intensive agricultural practices which have eventually led to the progressive depletion of soil nutrients. The abnormal growth in agriculture production has only been due to an excessive use of agrochemicals which have adversely affected the soil and water quality of the area. The contribution of agriculture to the requirements of health, nutrition as well as economical developments has been globally recognized [1]. Increased yield has been acquired with the development of newer high quality seeds and crops, applications of fertilizers and pesticides in excess amounts then the required ones, and using advanced agricultural machinery. Agricultural improvements have been the major sources of boon in meeting out the global requirements. Numerous issues however, have endangered criticism; the important ones are the environmental concerns including soil erosion, salinization and flooding of heavily irrigated soils, aquifers depletion, deforestation and environmental pollution due to the excessive use of pesticides and other agrochemicals [2-5]. The agrochemicals are indispensable in the modern agricultural technology as they significantly contribute in crop protection and pest control. Their application in the form of different formulations viz. dusts, sprays, wettable powders, flowables, emulsifiables concentrates, baits, etc. for achieving increased agricultural products, actually finds access in environmental segments such as lithosphere, atmosphere and hydrosphere through various natural processes. These chemicals including pesticides are reported to cause carcinogenic, mutagenic, reproductive anomalies and also affect various developmental processes [6-8].

These days, synthetic chemical pesticides and herbicides (e.g. carbamates and organophosphates) are widely used to combat crop loss. Such agrochemicals are associated with environmental pollution due to presence of toxic residues. Employing reduced-risk pesticides and herbicides based on plant essential oils, which are also biodegradable [9] may prove an excellent alternative. Pesticides have caused a great harm to humans and the environment. For environment and drinking water, the maximum admissible concentration of a single compound established by the European Union (EU) is 0.1 mg L^{-1} and 0.5 mg L^{-1} as maximum allowed for the total concentration of all pesticides [10].

2. Controlled Release Technology in Agriculture

"Controlled release (CR) is the permeation regulated transfer of an active ingredient from a reservoir to a targeted surface to maintain a predetermined concentration level for a specified period of time" [11, 12]. The comparative release profiles of conventional and CR assisted delivery of active agents are shown in **Figure 1** which clearly depicts how a CR formulation can maintain an effective level of agent for a longer and desired time.

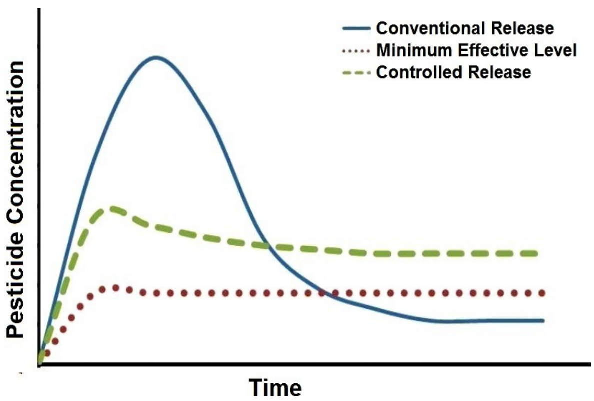

Figure 1: Theoretical pesticide active site concentrations from conventional and controlled release.

In the case of a conventional formulation, the AI is released with a higher concentration greater than the optimum level needed in short time duration. CR technology has been applied in agriculture, biomedical, food, pharmaceutical industries to deliver active substances such as pesticides, herbicides, fertilizers, biomolecules and drugs [13-17].

In most of the checked release formulations, the active agent is dispersed in or combined with polymeric matrices [18] through i) Physical mixing of an active agent with a polymer to yield a rate controlling device; ii) Chemical binding of the active agent to the polymer matrix to act as carrier and subsequent release of active ingredient is controlled by the chemical cleavage of polymer-active agent bond or by environmentally induced depolymerization. The choice of either method for achieving controlled release in a particular application depends on the release rate required, properties of the active agent and the cost [19].

Controlled release technology is used in crop so that environmental pollution can be reduced. It offers several advantages over the conventional methods of pesticide applications. CR technology has many applications in agriculture, where protection of crops from pests is required for extended period of time [20, 21]. Some of the advantages of this approach are worth mentioning such as, constant level of active agent, smaller doses, reduction of evaporative losses, reduction of phytotoxicity, decrease in environmental pollution, ease in handling and a steady rate over an extended period of time [22, 23]. The main objectives controlling the agrochemicals delivery are to achieve more effective therapies, less side effects, prolonged efficacy, enhanced safety and reliability of agrochemicals [24-27].

A safe pesticide formulation could be one which checks the availability of the active moiety at any point of time to be adequate for pest control and leave minimum residues on crops and in environment. Encapsulating technology provides us a handy tool which helps to achieve these chemicals in the polymeric matrix. The polymer encapsulated formulations are superior to non encapsulated commercial formulations in extending activity [28, 29], reducing evaporative and degradation losses [30], leaching [31], and dermal toxicity [32]. When the normal half-life of a potent pesticide is short, the release formulations are especially advantageous in comparison to conventional methods of application [33].

2.1 Advantages of controlled release technology

Delivery of an active agent at a desired rate and duration forms the very basis of CR technology and offers numerous benefits over conventional way of applications. The advantages of controlled release techniques may be summarized as below:

(i) In the traditional delivery systems, the active agents give maximum release in the initial duration of application and then the availability of active agent goes an increasing and almost acquires ineffective level at the end of the process. These problems can be solved by controlled release technology, which gives the uniform release amount upto the whole application period.

(ii) The use of agrochemicals used for controlling pests and weeds vegetation in traditional agricultural practices often results in spreading of active agent by runoff or wind and may be hazardous to animal beings and human. In CR technology, however, a much less amount of active agent is required for the purpose and, therefore may significantly cut down the exposure risks to human, animal and surrounding.

(iii) The CR technology is economically viable as less amount of active material is needed due to reduction in the number of applications to acquire the desired level of agricultural activity.

(iv) It also lowers results in reduction of phytotoxicity by lowering the high mobility of the pesticides in the soil, thus reducing its residues in the food chain.

(v) CR technology also gives the sufficient options to select pesticide for crops. In spite of these advantages, there are certain points that need to be considered prior to designing a CR formulation, as discussed below:

(a) It normally happens that the CR formulations are a little bit more costly than the conventional applications due to the costs of preparing and polymer(s) used in fabricating the formulations. This could, however be modified by using low cost naturally occurring polymers. Furthermore as repeated application of pesticide will not be required with CR formulations, the extra cost will be less compensated.

(b) In CR technology after the release of pesticide from the formulation, the polymer is blended to the soil and it may produce undesired consequences. Thus, to avoid these situations it is inevitable to use either degradable polymers or such polymers that could enhance the fertility of the soil after disintegration.

(c) It is also advisable to load two or more kind of agricultural active agents on a single polymer carrier so that multi way effects could be observed on the quality a quantity of the soil [34].

2.2. Polymers in Controlled Release Formulations

Polymer properties can be made more applicable to meet specific needs by varying the "atomic composition" of the repeat structure and by varying molecular weight. The polymer flexibility can also be varied through the presence of side chain branching and according to the lengths and the polarities on the side chains[35,36].

2.3. Types of Polymeric Controlled Release Formulations

Controlled delivery is one of the most enviable requirements from a carrier, which involves multi-disciplinary site specific or targeted approach.

a) Nanoparticles: Nanotechnology is known to involve the study and use of materials at an extremely small scale of few nanometers and exploits the fact that the same material might have very different properties at this ultra small scale than at the micro or macro levels. Nanoparticles vary in size from 10 to 1000 nm. The active ingredients (**Figure 2**) are dissolved, entrapped, encapsulated or attached to nanoparticles matrix depending upon the method of preparation [37, 38].

b) Nanocomposites: Nanocomposites are conventionally prepared by a judicious combination of organic polymer matrix and inorganic filler of nanodimension. The resulting hybrid materials exhibit high durability, high strength, design, light weight and process flexibility, used in so many industries including transportation, agriculture, aerospace, defense, sporting goods, food manufacturing, packaging and energy infrastructure sectors[39,40].

d) Carbon Nanotubes (CNT): CNTs are used as vehicles to deliver desired and useful agrochemicals into the seeds during germination that can protect them from the diseases. Since CNT is growth promoting, it will not have any toxic or adverse effect on the plant [41].

e) Mesoporous Silica Nanoparticles: Mesoporous silica nanoparticles have been extensively investigated as a delivery system. It is well known that mesoporous silica nanoparticles have porous and homogeneous nature, high pore volume, tunable pore structure, high specific area and physicochemical stability. Mesoporous silica nanoparticles help in delivering DNA and agrochemicals into isolated plant cells. Mesoporous silica nanoparticles are chemically coated and serve as containers for the plant as a genes delivering agent [42].

f) Nanosensors: The biosensor system is a useful and an ideal tool for online monitoring of agrochemicals and nerve agents. Bio analytical nanosensors are used to detect and quantify the minute amounts of contaminants like bacteria, viruses and toxic microorganisms etc. in agriculture and food systems [43].

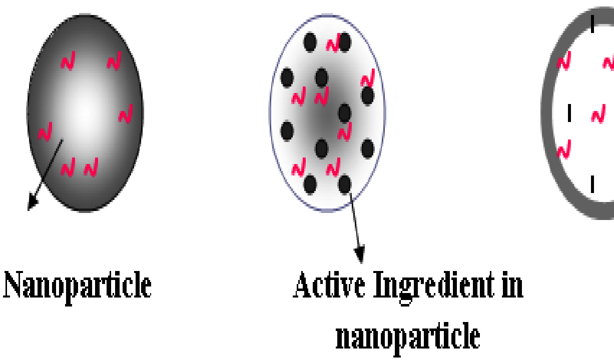

Figure 2: Polymeric nanoparticles for controlled release.

The AI release in this case is controlled by the transport rate of the active compound across the membrane (membranes can be porous or non-porous, and biodegradable or non biodegradable), that is, by the diffusion coefficient and the thickness of the layer (according to the Fick's law). These systems exhibit a very interesting zero order kinetic, a constant release rate independent of time [44].

2.4. Release from Biodegradable Systems

The biodegradation mechanism of AI release (as depicted in **Figure 3**) from biodegradable controlled release systems affects device performance substantially. The significant factor is the device design.

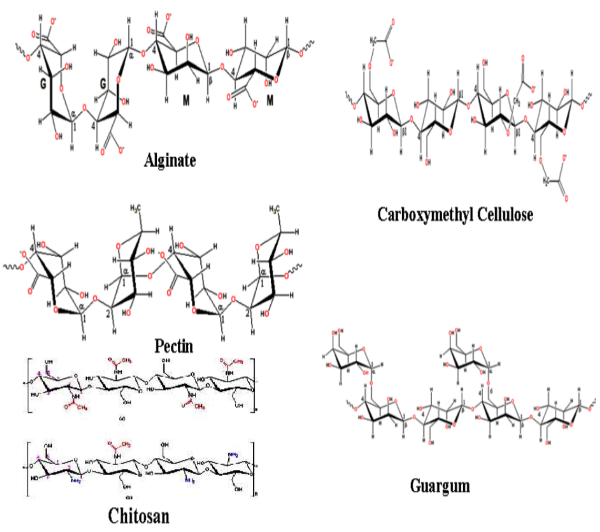

Figure 3. Selected biodegradable polymers commonly used for pesticide controlled release.

3. ENVIRONMENTAL CHALLENGES DERIVING FROM AGROCHEMICALS

Pesticides disappearance (95%) from soil by volatilization, leaching, surface run-off, and uptake by plants or the migration of invertebrates or small mammals with residues in their bodies is depicted in **Figure 4**. Comparable pathways of loss of pesticides from plants are that residues which may volatilize pass to the soil, in root exudates or be removed when the crop is harvested. Only the residues that remain in the plant or soil are metabolized, and often, for persistent pesticides, these represent only a small proportion of the whole.

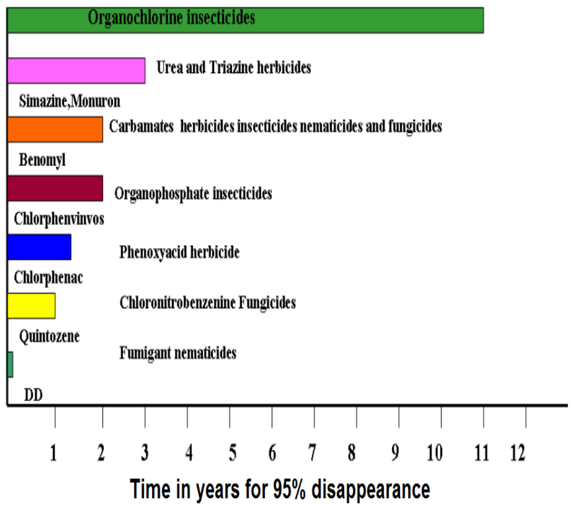

Figure 4: Pesticide disappearance (95%) from soil (time in years).

4. CONCLUSIONS

In this review articles, we have discussed the various agrochemicals and their controlled release effect. Various removal methods such as Nanoparticles, Nanocomposites, Carbon Nanotubes, Mesoporous Silica Nanoparticles, Nanosensors have been also reviewed. It was found in survey of literature biodegradable polymers widely used in controlled release technology due to their degradable nature and non polluting waste material.

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