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Polymer indispensability in controlled release pesticides

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ABSTRACT: Polymers are used in pesticide formulations, for controlled pesticides release. Protein such as Gelatin, casein and amino acids are another major class of natural polymers used in the controlled release formulation of pesticides. However, Polymers like methyl isocyanate, methyl chloride alcohol and σ nitrocellulose, σ nitrobengene, σ nitrochlorobenzene are used for making carbofuranpesticide. For mancozeb, maneb and zineb, pesticides, ethylenediammes and carbon disulphide are the raw materials. Synthetic polymers used in pesticides, insecticides, herbicides are chlorinated hydrocarbons, organic phosphates (organophosphates) and carbamates. Types of synthetic polymer pesticides include the organochlorides, organophosphates, carbamates and pyrethenoids. Smart polymeric systems have extensively contributed to the advancement of the agricultural industry by increasing the efficiency of pesticides, insecticides and herbicides. Such polymers which can be functional and superabsorbent also serve as controlled released pesticides in agriculture. Polymer additives regulate pesticides droplets deposition on hydrophilic and hydrophobic plants. Both synthetic and natural polymers are being used to develop pesticides formulations depending on the needs and suitability. Polymer Nano carriers for pesticides are been developed, these include chitosan, alginates and starch, such polymer pesticides are known to exhibits a high stability phenomena. Polymer additives, composed of negatively charged polymer such as polyacrylic acid and a positively charged polymer such as poly – ethyleneimine are mixed with pesticides to solve some pesticides problem. Degradable and biodegradable polymeric Nano particles are in common use, because they are easily decayed. Natural biodegradable polymers employed in pesticides include proteins, carbohydrates (chitosan, alginates, starch, carboxymethyl cellulose), ethyl cellulose and the synthetic polymers such as polyethylene glycol, polylactic acid, polycaprolactone, polyhydroxybutyratewhich are easily degradable.

Keywords: Pesticides, polymers, superabsorbent, controlled release

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INTRODUCTION

Modern farming methods cannot succeed without the employment of pesticides. The main reason for the making of pesticides is for the maximum biological activity of agricultural based chemicals, while, also producing a very authentic and safe document, easy to utilize. Orthodox formulations of pesticides include granules, powders, dispersible, liquids and dusts. These were presented in forms such as emulsions and suspensions (Parmar and Tomar, 2004). These forms of formulations are still the norm and versatile. However, there are challenges of environmental hazards, erosi on, types of soil most suitable i.e clay, sand or loam, evaporation, biodegradation and chemical reactions. Other problems include over-dosing, environmental pollution and groundwater contamination, leaching, surface migration and so on. The use of polymers in recent formulations of pesticides has ameliorated this problem. The advancement in controlled – release (CR), pesticides and fertilizers formulation has seen the use specialized polymers to optimize the benefits of agro-chemicals and reduce costs and hazards (Kydonius, 1980). CR technology uses a polymer containing a biologically active ingredient, which is release into the target site at a relatively constant rate over a pre-determined time frame. This determined time reduces the risk of wastages and optimizes the effect of the pesticides. Such effectiveness and release of the active ingredient from the controlled – release polymer depends on the physical and chemical parameters of the polymer viz biodegradability, permeability, environmental stability degradation and stability. Such polymers are also being engaged as encapsulating agents for or as a backbone for chemical (pesticidal) groups. For the olden days, pesticides were usually fastly and hence, very quickly lost resulting wastes in and lots of environmental pollution. However, with the advent of controlled release technology, there are great improvements efficiency of pesticides, reduce leaching loses to environmental forces. Controlled release reduces overdosing and achieves a good pesticide plant balance for optimum crop yields. This technology assures a target site delivery over a predetermined time frame, achieves effective levels of pesticides throughout the growing season, both the vegetative and reproductive stages of the crops and even to the next growing season at the normal / acceptable levels. A controlled release technology based formulation is usually a zero order release reaction and is the ideal process with optimum effect and no harmful side effects (Kydonius, 1980).

Cultural practices such as pre-planting, planting proper and post planting are usually carried out with processes and practices that entails the over-exploitation and abuses of the natural resources and environment (FAO 2011) such resources include excessive use of water, agricultural chemicals such as pesticides, herbicides, insecticides and fertilizers. Due to the high and increasing requests for good water, irrigation high cost of agro-chemicals and their dangers to man, animals and the environmental pollution effects accompanying such practices and the unsustainability of such method – there is the very urgent need to better the soil conditions (structure, fertility) as well as excellent water and plant management. The aim of this paper is to highlight the very possibility of special polymers in regulating the use, and for a more judicious controlled and release of agro-based chemicals in order to reduce the pollution of the environment and costs (Ekebafe et al, 2011).

This study presents the ample opportunities available to increase the utilization of controlled release chemicals in agriculture by X-raying some of the work done and exploring the use of chemical in technically, socially, environmentally, economically sustainable ways. It also looks at the main objective of producing smart and intelligent polymers with biodegradable and renewable characteristics and traits for diverse agricultural uses in farms and farming environments and settlements (Priscila et al, 2017).

MATERIALS AND METHODS

Artificial or synthetic and natural materials are usually employed in this study. Artificial or synthetic such as Polyvinyl Alcohols (PVAs), The Polyamides, The Polyethylene, The Polyethylene Glycols etc., Natural such as Starch, protein, Chitosan etc.

Some artificial / synthetic polymers

Such polymers used in controlled release pesticides are discussed below.

The polyvinyl alcohols (PVAs) based

This is a crystalline polymer with OH^- (hydroxyl group). It is made by the hydrolysis of polyvinyl acetate, which is a polymerized product of vinyl acetate. Glutaraldelyde cross – linked polyvinyl alcohol / alginate - montmorillonite (PVA / Alg – MMT) nanocomposite was used to develop controlled release formulation for a botanical pesticide, called NeemAzal (Rashidzadeh *et al 2014*).

The polyamides based

The polyamides based controlled release technology utilizes cross linked polyamide (nylon) encapsulated methyl parathion. Others include carbofuran, methonyl, monocrotophos, phosphemidon – insecticides are all active against the mahogany stem borers, Hypsiphylagrandella (Allan *et al 1974)*.

The polyethylene based

This polymer comes in different forms such as low – density polyethylene (LDPE), high – density polyethylene (HDPE). Though, other forms exist, these two variants are the most common. HDPE is usually very suitable for packaging of liquid pesticidal formulations due to its excellent physical and chemical resistance and semi – crystalline nature. A good example is methyl parathion and diazinon with HDPE (Jarvinen and Tanner, 1982).

The Polyethylene Glycols Based

This polymer has the molecular formula, {Ho – (CH_2 $CH_2O)_n$ – H). Its molecular weight varies from a few hundreds to even thousands and very soluble in water and also hydroscopic and finds a wide use in various pesticidal formulations industry – wise. Its main forms as a surfactant and base polymer for seed coat formulations. Polyethylene glycol Nano micelles are used for the encapsulation of carbofuran, a systemic insecticide – nematicide (Shakil *et al 2010).*

The polyvinyl chloride (PVC) based

This polymer is a semi crystalline with good physical and chemical resistance and strength – to – weight ratio. PVC is used in chlorpyrifos, which provides extended insecticidal activity for about 22 – 24 weeks compared to emulsions formulations with 1 – 2 weeks activity (Nelson *et al, 1970*).

The poly vinyl pyrrolidone (PVP)

This polymer has been used as a dispersant with excellent water fastness parameters.

Some natural polymers used in the formulation of controlled release of pesticides

Starch based

Starch is a homopolymer, a homopolysaccharide, made of mainly two types of chains. While amylose is a linear polymer of glucose units connected by ℵ- (1, 4) glucossidic bonds, and amylopectin is a branched polymeric structure of glucose units connected by ℵ - (1, 4) and ℵ - (1, 6) glucossidic bonds. The great advantage of starch is its biodegradability, versatibility and cheapness. The incorporation of natural rubber latex in the starch xanthate microcapsule led to the improvement in the slow – release properties. Starch is used to prepare the herbicide, Trifluralin, utilizing auto-encapsulation methods (Trimell and Shasha, 1988). Starch – borate complex, made by boiling starch (corn or cassava, potato, yam, cocoyam, millet) in boric acid solution was employed to encapsulate an organophosphate pesticide, diazinon (Brown, 1991).

The alginates based

Alginate is a linear polysaccharide, composed of 1 – 4 bonds of B – D – manuronic acid and ℵ - L –guluronic acid. Alginate is gotten from the brown algae. Aluminum alginate, sodium alginate and ammonium alginateand starch – based microsphere was used in controlled release of chlorpyrifos. Alginates based isoproturon, imidaclopridcyromazine and inorganic bentonite clay, anthracite and charcoal have all been investigated with promising results, for their use in controlled pesticides release (Cespedes, 2007; Garrido – Herrera, 2006).

The cellulose based

Cellulose is a giant polymer composed of B – D glucopyranose units, linked by B – (1, 4) glucosidic chemical bonds. It is cheap, common, versatile and very much biodegradable. It is also very much biocompatible in nature. Such cellulose derivatives include, carboxyl methyl cellulose (CMC), ethyl cellulose, methyl cellulose have all being employed in controlled release pesticides. Granules of chlorosulfon herbicides were prepared with ethyl cellulose and addition of a plasticizer (dibutylsebacate) resulting in 100% encapsulation efficiency (Cepedes *et al 2007*).

The polylactic acid based

This polymer is aliphate polyester. It is also a biodegradable biopolymer gotten from the condensation polymerization of lactic acid. The physical entrapment of pesticides in pulverized poly lactic acid was reported to develop slow – release formulations of sodium salt of 2, 4 – dichlorophenoxyacetic acid (2, 4 – D) (Liu *et al., 2016*).

The cyclodextrin based

The cyclodextrins are polysaccharides composed of ℵ - D – glucopyranose units connected by ℵ - (1, 4) bonds. The modification of starch by enzyme activity yields ℵ - cyclodextrin made of 6 (six) glucose units, B – cyclodextrin (seven units) and Y – cyclodextrin (eight units). Cyclodextrin is used in controlled delivery of pesticides such as 2, 4 – D atrazine, cavacrol, 2, methyl – 4 – chloropheneoxyactic acid (MCPA) (Fernandes*et al 2014*).

The chitosan based

The natural polymer chitosan is a cationic polyelectrolyte polysaccharide derived from the deacytylation of chitin. It is made up of varying amounts of B (1 – 4) – linked 2 – acetoamido – 2 – deoxy – B – D – glucopyranose and 2 – amino - 2 – deoxy - B – D – glucopyranose. Due its hydrophobicity biocompatibility, biodegradability, bioadiversivity and great abundance in nature, chitosan finds a very extensive application almost of fields of human endeavour: technology, science, food, electronics, engineering, medicine, pharmacy, farming – mainly in mulching and crop protection. Chitosan hasantimicrobial qualities such as fungicidal, bactericidal and can induce plant defence mechanism. Chitosan (cationic) and alginate (anionic) based formulation of etofenprox was found to be very effective against the pest spodopteralitura, with imidacloprid, against the insect Martianusdermestoide (Hwang et al 2010; Guan *et al., 2008*).

The lignin based

The system of pesticide involving the formulation of 2, 4 –

D was prepared by melting the 2, 4 – D in water soluble lignin from sugar cane bagasse and wood. The diffusion of diuron herbicide was reported from a granular formulation, made by using alkali lignin from sugar bagasse, pine and eucalyptus woods. These were used to develop the controlled release formulation of chloridazon and metribuzin effective against a wide range of fungi, bacteria and other microbes causing diseases (Fernandes C. J. *et al 2020*).

METHODOLOGY

The concept of controlled – release of chemicals has been a serious issue since the 1960s. Dertli and limit in 1960 and Allan et al in 1971, used the method of membrane encapsulation to study the controlled – release of chemical. In the system of membrane encapsulation, a chemical – pesticide, fertilizer, herbicide is embedded or hidden inside the membrane or body of another polymer.

This then, controls or metres the release of the chemical as and at when due. The acrylic-based organic polymers such as acrylamide-based gets (Allan et al, 1971). Other polymers used include natural rubber, polyethylene, copolymers of acrylic acid polyesters and cyclopentadiene, unsaturated fatty acids, polysaccharides and cellulosic (Puoci et al, 2008), starches, organic polymers, inorganic materials, hybrid materials, and composites. Examples include, pentachlorophenol, 2, 4 – dichlorophenoxyacetic acid, used as proprietary herbicides (Kashyop et al, 2015), fertilizers with NPK, urea, KNO_3, CO_2CO_3, micro- and macro- nutrients fertilizers such as phosphorus, potassium, manganese, zinc, copper, molybdenum, boron and others. The great newsis that through membrane encapsulation, these chemicals can be regulated according to agronomical need such as soil, crop and weather type (Puoci et al, 2008). Pesticides such bifenthrin, tebuconazole, chlorpyrifos, atrazine etc. (Roy et al., 2014). Table 1 shows some process and methods applied in controlled – release of chemicals. The fabrication of controlled – released materilas has been entirely with synthetic and artificial polymers. However, recently, attention is now focused on the use of biodegradable composite polymers as materials for the controlled – release of farming chemicals in the soils (Roy et al, 2014 and Ibrahim et al 2016).

Liong et al. (2007) also used the method of entrapment of NPK inside a poly (acrylic acid co – acrylamide) / Kaolin clay super absorbent composite. Clay was used to reduce cost and improve swelling ability. Temperature was kept increasing and higher, solubility observed and improve biodegradability of both materials (Liong et al., 2007, Garrido et al, 2014 and Ge et al., 2022).

RESULTS AND DISCUSSION

The degradation of organic and inorganic chemicals (polymers) is referred to as biodegradation. It is a process in which complex molecules and compounds are converted into mineralized forms and redistributed through cycles such as the carbon cycle, nitrogen cycle and the sulphur cycle, by the action of soil micro and macro organisms. (Shuterland et al., 1997). The use of natural and biodegradable polymers are a pre-requisite to overcome many problems concerning the environmental and green aspects of polymer applications in controlled release of pesticides (chemicals generally) in agriculture. Also, synthetic polymers are most popularly used in farming as intelligent agrochemicals and as super absorb results in severely huge quantities of non-biodegradable wastes and soil contamination resulting large scale soil and environmental pollution. (Watanabe et al 2009, Ge, et al 2002). Another big challenge is to find a polymer with both long accurate release context and a high rate of biodegradation under the mild conditions of farming fields. As Shuterland et al 1997 have proved, the microorganisms naturally available in the soil are not usually able to biodegrade the added polymers. Hence, it is necessary to conduct much research in order to increase the rate of biodegradation.

Shuterland et al., (1997), Watanabe et al. (2009) and Ge, et al. (2002) agreed that systemic and controlled release of pesticides was the best practice for optimum use of such chemicals. Dertli, and Lunt in the 60s, and Allan et al in 1971 after a series of studies and experimentation concluded that controlles release was useful using embedded or hidden methods and a series of different materials. Roy et al, 2014, Ibrahim et al, 2016 and Kashyap, et al, 2015 and earlier on, Pouci et el, 2008, all use both synthetic and natural materials, with concentration on biodegradable materials for controlled release of farm chemicals. Rashidzadeh et al, 2014 and Shakil et al, 2010, both worked on polyvinyaccohols and polyethyglycols as formulations and also acting as carriers in controlled released chemicals and came to the same conclusions and similarly Brown, 1991 earlier found out a similar fact and also Cespedes, 2007, Garrido – Herrera, 2006 working with polysaccharides. This was also corroborated by Lui et al in 2016. Hwang et al, 2010 and Guan et al, 2008 working with Chitosan agreed with Fernandes et al, 2014 and Fernandes – Perez et al, 2015 worked with Cyclodextrin and Lignin respectively.

Conclusion

From the brief study of the use of polymers in controlled release (CR) of pesticides, there is much ample room and opportunities to enhance the application of polymers

Table 1. Polymers used into slow/controlled-release materials.

Agrochemical used	Polymer used
Urea	Chitosan
	Polyhydroxybutyrate (phb), ethyl cellulose
	Polyethylene, polyvinyl acetate, polyurethane, polyacrylic, polylatic acid
KH_2PO_4	Chitosan, gellan gum
NPK	Chitosan
	Cellulose, natural gum, rosin, waxes
	Paraffins, ester copolymers, urethane composites, epoxy, alkide resins, polyolefines,
$CaH_4P_2O_8$	Chitosan
KNO_3	Chitosan
	Chitosan-clay (montmorillonite)
	Xanthan
Paraquat ($[(C_6H_7N)_2]Cl_2$)	Alginate, chitosan
Hexazinone ($C_{12}H_{20}N_4O_2$)	Chitosan – clay
Clopyralid ($C_6H_3Cl_2NO_2$)	(montmorillonite)
2, 4-d ($C_8H_6Cl_2O_3$)	Polysaccharides
2-chloro-;4-chloro-	Cellulose, agarose, dextran, alginates, carrageenans, starch, chitosan, gelatin,
2,4,5-Trichloro- phenoxyacetates	Albumin
Validamycin ($C_{20}H_{35}NO_{13}$)	Polystyrene, polyacrylamide, polymethylacrylate, polyamides, polyesters,
Bifenthrin ($C_{23}H_{22}ClF_3O_2$)	Polyanhydrides, polyurethanes, amino resins, polycyanoacrylates
Chlorpyriphos ($C_9H_{11}Cl_3NO_3PS$)	
Bifenthrin ($C_{23}H_{22}ClF_3O_2$)	
Azadirachtin ($C_{35}H_{44}O_{16}$)	

in agriculture. However, such use must be done in an environmentally, technically, socially, economically friendly and sustainable way. Many opportunities exist to produce intelligent polymers with biodegradable and renewable properties for controlled release of not only pesticides, but a whole range of agro – industrial chemicals.

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