

I. INTRODUCTION

The use of agricultural pesticides has increased dramatically during the past two decades for the control of insect pests, weeds and diseases in Egypt because pesticides are the most-effective means of pest and weed control, allow the maintenance of current yields and so contribute to economic viability. Nevertheless, approximately 90% of agricultural pesticide application never reaches its target organisms but is, instead, dispersed through the air, soil and water (**Moses *et. al.*, 1993**). In addition, many soil-applied pesticides (herbicide and nematicide) are also intentionally introduced into the soil environment for the control of weeds, soil borne pests and pathogens, which results in the accumulation of their residues and metabolites in soil at unacceptably high levels (**Redondo *et. al.*, 1997, Gamo'n *et. al.*, 2003**).

Concern pesticide adverse effect, pesticides are bio-accumulative and relatively stable (can persist for long periods in the eco-system). Also, they are transported into groundwater or leached to the surface water.

How long the pesticide remains in the soil depends on how strongly it is bound by soil components, as well as, soil type, pH, organic content, mineral ion content, moisture content, the nature of the soil colloids, the flow of liquid and air through the soil, the amount of cultivation and plant growth present, etc., (**Hirahara *et. al.*, 1997; Jones and Norris 1998**).

Herbicides are anionic and only weakly adsorbed by soil, thus, they have the potential to leach and move into deeper soil layers (**Nicholls *et. al.*, 1987**) and this may have important implications which increase with increasing pH and with decreasing organic mater content (**Hay, 1990 and Saha *et. al.*, 2002**). As sulfonylurea herbicides are used extensively for weed control in cereals which can they may injure rotational crops. Sulfonylurea herbicides degraded slowly particularly persist in the soil for more than one growing season because of their slow rates of loss, when soil pH is greater than 7-7.5 (Egyptian soil), where the microbial

degradation and chemical hydrolysis are decreased (**Fredrickson and Shea, 1986**).

Nematicides remain an important means of controlling nematodes in different attacked cultivations. Cadusafos is an organophosphorus nematicide and it is the most effective nematicide comparing to carbosulfan, and triazophos, (**Meher *et al.*, 2010**).

In this respect, many workers tried different removal, degradation, bioremediation and physicochemical methods for organic contaminants elimination from soil. Soil amendment is an important physicochemical process that strongly management of organic contaminants transport and fate in the environment. Many reports are mentioned to many adsorbent materials which are used to remove different pollutants, (**Cowan *et al.*, 1991; Gupta, 1998 and Kesaoul-Qukel *et al.*, 1993**). For example, Pure-form ashes of wheat and rice residues and fly ash were highly effective adsorbents of the herbicides diuron (**Yang and Guangyao, 2003**), and metribuzin (**Majumdar and Singh, 2007**), respectively. Also, sugarcane bagasse fly ash was affective materials to remove 1,1- dichloro-2,2-dichlorophenyl ethane (DDD) and 1,1-dichloro-2,2-dichlorophenyl ethylene (DDE) from wastewater (**Gupta and Ali, 2001**), and can accelerate lindane degradation by microbial activity, (**Abhilash and Nandita, 2008**). In addition, gypsum can be cost-effective way to improve soil pH or structure. Calcium in gypsum improves soil structure by replacing sodium on the exchange surfaces of clay (**Pluske, 2005**), and can reduce soil pH which allow a more rapid dissipation of pesticides (**Williams, 1998**).

Therefore the present work was conducted to determine the potentials and elimination efficiency of some natural additive materials; sugarcane bagasse, rice straw and gypsum on leaching of organic chemicals (tribenuron-methyl and cadusafos) that could contaminants the groundwater. In addition the side effect of the addition materials on plant growth was taken into consideration.

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LIST OF ABBREVIATION

TBM	: Tribenuron-methyl
DMSO	: dimethyl sulphoxide
DFA	: Day From Application
Chl. a	: chlorophyll (a)
Chl. b	: chlorophyll (b)
Chl. t	: chlorophyll total
f.w.	: fresh weight
d.w.	: dry weight
GLC	: Gas- Liquid Chromatography
HPLC	: High Performance Liquid Chromatography
ppb	: part per billion
I.U.	: International Unit
O.M	: Organic Matter
a.i.	: active ingredient
G	: Granule
DF	: Dust Fine
DDT	: 1,1,1-Trichloro-2,2-dichlorophenyl ethane
DDD	: 1,1- dichloro-2,2-dichlorophenyl ethane
DDE	: 1,1-dichloro-2,2-dichlorophenyl ethylene
RFD	: recommended field dose
g	: gram
µg	: microgram
mg	: milligram
Kg	: Kilogram
OCI	: Organochlorine insecticides
PVC	: Poly Vineyl Chloride

II. REVIEW OF LITERATURE

2. 1. Elimination of some organic pollutants from soil:

2. 1. 1. Factors affecting pesticide persistence, degradation and leachability in soil:

The time long that herbicide remains its active in the soil is called “soil persistence” or “soil residual life. Many factors determine the long of time herbicides persist. Most factors fall into three categories: soil factors, climatic conditions, and herbicidal properties. These categories strongly interact with each other. Herbicides vary in their potential to persist in the soil. Some herbicide families that have persistent members include the triazines, uracils, phenylureas, sulfonylureas, dinitroanilines, pigment inhibitors, imidazolinones, and certain plant-growth regulators (Hager and Refsell, 2008).

The soil factors affecting herbicide persistence fit into three categories: physical, chemical, and microbial properties. Soil composition is a physical factor that measures the relative amounts of sand, silt, and clay (the soil texture) and the organic-matter content of the soil. Chemical properties of the soil include pH, cation-exchange capacity (CEC), and nutrient status. The microbial aspects of the soil environment include the type and abundance of soil microorganisms present. Soil composition affects herbicide phytotoxicity and persistence through adsorption, leaching, and volatilization. Chemical breakdown and microbial breakdown, (two major herbicide degradation processes), are often slower in soils of higher pH. So although decreased adsorption of triazine herbicides occurs in soils of higher pH, there is also less breakdown activity. Therefore, these herbicides are more available for plant uptake for a longer period on soils of higher pH. Certain members of the sulfonylurea group (chlorsulfuron and chlorimuron) can also persist in higher-pH soils because rates of chemical breakdown are decreased. Low pH affects the persistence of clomazone and the imidazolinones

(imazaquin and imazethapyr). Soil pH has little effect on the persistence of other herbicides (**Hager and Refsell, 2008**).

Herbicide degradation rates generally increase with increased temperature and soil moisture because both chemical and microbial decomposition rates increase under higher temperature and moisture conditions. Sunlight is another important factor in herbicide degradation. Photodegradation, or decomposition by light, has been reported for many herbicides. The dinitroanilines (trifluralin and pendimethalin) are sensitive to light degradation (**Hager and Refsell, 2008**).

Pesticide degradation is the breaking down of toxic pesticides into nontoxic compounds and in some cases down to the original elements from which they were derived. The first and the most common type of degradation is called microbial degradation and carried out in the soil by microorganisms, especially fungi and bacteria (**Vargas and Jr., 1975**). Soil conditions such as moisture, temperature, aeration, pH, and the amount of organic matter affect the rate of microbial degradation because of their direct influence of microbial growth and activity. Rapid microbial degradation is more likely when the same pesticide is used repeatedly in a field. Repeated applications can actually stimulate the buildup of population of these organisms effective in degrading the chemical. As the population of these organisms increases, degradation accelerates and the amount of pesticide available to control the pest is reduced (**Williams, 1998**).

Walker et al., (1989) measured adsorption and degradation rates of chlorsulfuron and metsulfuron-methyl in soil taken from depths of 0-20, 20-40 and 40-60 cm at eight sites. Adsorption of both herbicides was negatively correlated with soil pH, and positively correlated with soil organic matter content. When two soils with very high organic matter were excluded from the calculations, the correlations with organic matter content were no longer statistically significant but those with soil pH were affected only slightly. Degradation rates of both herbicides generally

decreased with increasing depth in the soil and were positively correlated with microbial biomass and negatively correlated with soil pH.

Chemical degradation is the breakdown of pesticides by processes that do not involve living organisms i.e. temperature, moisture, pH, and adsorption. According to (**Thirunarayanan *et al.*, 1985**), there was an inverse relationship between pH and degradation rate on adsorption of chlorsulfuron herbicide, with decreasing moisture and temperature the chlorosulfuron degrade more slowly.

Janjic and Jevtic (1990) discussed the factors that influence herbicide transformation in soil. Soil properties comprise 1 group of these factors; they include the physical (e.g. texture and OM content) and chemical (e.g. pH and CEC) properties of the soil, and microbiological characteristics such as the density and type of microorganism present.

Sarmah *et al.*, (1998) showed that in acidic soils, sorption of chlorsulfuron, metsulfuron-methyl, and triasulfuron is strongly influenced by the soil temperature, clay content and particularly, organic matter content. The principal modes of degradation are acid hydrolysis and microbial degradation. Hydrolysis is rapid under acidic conditions (pH 4-7) and the data suggested it is likely to be very slow in alkaline soil. Data from other countries suggested that the half-life of chlorsulfuron be influenced by variations in the temperature and water content of soil.

Spark *et al.*, (2002) studied the effect of the solid and dissolved organic matter fractions, mineral composition and ionic strength of the soil solution on the sorption behaviour of pesticides. A number of soils, chosen so as to have different clay mineral and organic carbon content, were used to study the sorption of the pesticides atrazine, 2,4-D, isoproturon and paraquat in the presence of low and high levels of dissolved organic carbon and different background electrolytes. The sorption behaviour of atrazine, isoproturon and paraquat was dominated

by the solid state soil components and the presence of dissolved organic matter had little effect. The sorption of 2, 4-D was slightly affected by the soluble organic matter in the soil. However, this effect may be due to competition for adsorption sites between the pesticide and the soluble organic matter rather than due to a positive interaction between the pesticide and the soluble fraction of soil organic matter. It is concluded that the major factor governing the sorption of these pesticides is the solid state organic fraction with the clay mineral content also making a significant contribution.

Karpouzas *et al.*, (2007) Showed that Fosthiazate is an organophosphorus nematicide. The leaching of fosthiazate was investigated in columns packed with three different soils which represented situations of high (site 2), intermediate (site 1) and low (site 3) leaching potential. The recommended dose of fosthiazate was applied at the surface of the soil columns and fosthiazate fate and transport was investigated for the next two months. Fosthiazate concentrations in the leachate collected from the bottom of the columns packed with soil from site 2 exceeded 0.1 $\mu\text{g l}^{-1}$ in most cases. The results of the current study further suggest that fosthiazate is mobile in soil and can leach under conducive soil conditions like acidic soils with low organic matter content.

The chemical properties of herbicide affect its persistence, as will as; important factors include water solubility, soil adsorption, vapor pressure, and susceptibility to chemical and microbial alteration or degradation (**Hager and Refsell, 2008**).

Estévez *et al.*, (2008) showed that the long of pesticide remains in the soil depends on how strongly it is bound by soil components and how readily it is degraded. It also depends on the environmental conditions at the time of application, e.g., soil water content. There seems to be a great potential to develop microbial derived pesticides, which are effective,

reliable and have a low environmental risk. In addition, new application techniques, for example precision band spraying, can reduce the dose, which can be a very effective way to minimize transport and emission but also to avoid a build-up of resistance in target organisms. Improved formulations will also be needed to reduce off-target deposition, improve retention on target, and enhance uptake and translocation.

The amount of herbicide that moves away from the area of application will depend on the physico-chemical properties of the chemical and agroclimatic characteristics of the target site. Under average conditions, the amount of herbicide lost by movement from a soil profile is typically < 0.1 % to 1 % of the applied mass but, under certain localized circumstances, can reach up to 5 % or greater. Leaching, drain-flow and surface run-off are the main pathways responsible for herbicide movement within soils, **(Carter, 2000)**.

On the other hand, sulfonylureas herbicides are considered relatively mobile compounds in soil and their mobility increases with increasing pH and decreasing soil organic matter, according to **(Beckie and McKercher 1990; Srivastava *et al.*, 2006)**.

Olvera-Velona *et al.*, (2008) showed that ecotoxicological impacts of organic pesticides on soil and aquatic ecosystems depend primarily on their behavior in soils. Here, the sorption behavior of two organophosphorous insecticides, parathion and cadusafos, was studied in three agricultural soil samples from central Mexico, Vertisols and Andosols. The results show that cadusafos was less sorbed by the various soils compared with parathion. Cadusafos exhibited a greater reversibility of sorption than parathion in both soil types. Time-dependent sorption was quantitatively significant, leading to a rapid decrease in the concentration of available insecticide. This finding is partly due to the formation of non-extractable, bound residues. The decrease in the available concentration of both insecticides was greater in the Andosol compared with the Vertisols. Soil organic matter clearly influenced the

sorption behavior and availability of parathion. On the other hand, the sorption of cadusafos was more influenced by other soil properties such as clay content and cation exchange capacity.

Aktar *et al.*, (2009) investigated the leachability of three herbicides, two from dinitroaniline group (Pendimethalin, Benthocarb) and one from thiocarbamate group (Oryzalin) through soil columns and their contribution in ground water contamination. Soil column loaded with herbicides and after 30 days soil samples were analyzed from each segments (i.e. 0-6, 6-12, 12-18, 18-24, 24-30 cm). The results obtained reveal that the residues of three herbicides were predominantly confined to the upper soil layer (0-6 cm). Comparatively, low mobility of these herbicides in soil could be due to strong adsorption of these chemical to soil colloids. The chance of leaching of Benthocarb is less than other two herbicides. Therefore, the power of ground water contamination is negligible for Benthocarb than dinitroaniline group of herbicide.

El-Shafei *et al.*, (2009) illustrated the adsorption of cadusafos on two types of soils: clay loamy and sandy collected from two regions around the Nile Delta in Egypt. The adsorption process is fast reaching equilibrium in 60 min, decreases with increasing soil mass and independent on pH in the range 3–11. The experimental results were well fitted to linear partition model, and to a lesser extent to Freundlich non-linear model, Temkin and Dubinin–Radushkevich models. Water movement taking place more readily in sandy soil caused increased uptake relative to the case of clay soil. The higher uptake in sandy soil denotes that cadusafos may be mobile with a potential to leach and eventually pollutes ground water and surface water.

2. 1. 2. Background methods for pesticide elimination from soil:

Boul *et al.*, (1994) concluded that agricultural practices as flood irrigation, tillage, and superphosphate application, commonly used to increase productivity have beneficial side effects in reducing the levels of 1,1,1-Trichloro-2,2-dichlorophenyl ethane (DDT) residues in the soil compared to the control. Losses the levels of DDT residues due to microbial or photochemical breakdown, volatilization, and/or binding in a zone with higher organic matter may also have contributed to the lower residue concentration.

Bhattacharjee and Dureja (1999) showed that the sulfonylurea herbicide, tribenuron-methyl was readily photodegraded in aqueous solution under sunlight and UV light. The rate of photodegradation of tribenuron-methyl in different types of water followed first-order kinetics with significant correlation coefficient, increased with increase in pH and was also dependent upon the dissolved impurities.

Erman (2000) determined the rate of decomposition and nitrogen mineralization of plant residues in soil under laboratory conditions. The experiment consisted of six treatments: control, industrial tobacco residues, rice straw, rice straw + mineral nitrogen, rice husks and rice husks + mineral nitrogen. The plant materials were added at a rate of 2000 mg/kg and the amount of NH_4^+ -N completed the C:N ratio of the added materials to 12.5. After adding the plant material the following measurements were carried out: soil respiration measurements 14 times, dehydrogenase activity 14 times, mineral nitrogen (ammonium and nitrate). The results show that the C:N ratio was found to affect the net mineralization and nitrogen mineralization under the present conditions for decomposition of plant residues. Mineral nitrogen addition is conducive for short-term decomposition when the C:N ratio is large.