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Radiation Degradation Mechanism of some Pesticides in Sewage Wastewater

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Abstract: The characterization of DDT and DDE pesticides existing in wastewater was investigated. The determination of these pesticides was carried out by GC, HPLC and conductivity techniques. The results showed that the concentration of these pesticides is among the international range as a function of months.
The gamma radiation degradation of 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT), and 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE) dissolved in n-hexane was studied. DDT and DDE produced DDD and 2,2-bis(4-chlorophenyl) chloroethylene (DDMU) respectively. The degradation of these two former compounds was larger in iso-octane than in n-hexane or acetone. DDD, DDE and many DDMU would degrades to carboxyl group at 25 KGy.
The kinetic of the radiation degradation reaction of these pesticides, as a function of absorbed dose, illustrated that the first order reaction could be applied to explain the mechanism of the degradation reaction. The reaction starts slowly then accelerates it rates to reach a saturation value.

Keywords: Radiation effect, Pesticides, Extraction, Kinetic of radiation degradation.

1 Introduction

Environmental pollution is now recognized as a significant concern worldwide, while industrial sources are most common, other sources can also be significant [1]. Many of the contaminants biodegrade very slowly and may have adverse effects on humans and ecosystems [2]. In many areas of the world, water is the limiting resource necessary for successful growth and economic stability. It is know that water considered as one of the most significant obstacles to development in the Arab region [3]. Therefore, a strategy is being recommended that is beneficial wastewater reuse to protect what is left of this natural resource [4-6].
Pesticides are a mixture of materials that are used to prevent any pest, or to start to combat and eliminate it, including disease vectors of humans, animals or plants that enter any form during food production or during the cultivation of agricultural products [7].
Pesticides were not widely used in the nineteenth century. Rather, they were inorganic compounds (arsenic compounds and copper compounds). The use of synthetic organic pesticides began since the properties of the most important organic chlorine compounds (DDT) were discovered in 1939 by the scientist Müller [8]. The use of pesticides has expanded during the last four decades, which has contributed to protecting humans from deadly diseases and many of their pathogens transmitted by insects. Pesticides have also contributed to increasing agricultural production and achieving food security programs as a result of reducing crop losses due to pests. However, despite the great benefits that they have achieved, pesticides have caused great damage to the components of the environment. Therefore, their consumption must be rationalized and used rationally [9].

Chemicals introduced into the environment are exposed to many weathering and biological forces, all of which could alter the nature of their residues [10]. Recent studies indicate that pesticide contamination is systematically invading all the segments of our biosphere [11]. This can be considered as a consequence of the evolution of human activities in our modern societies.

Non-point source pesticide pollution can enter streams and rivers via three main routes; leaching [12], spray-drift and run-off [13]. Everts [14] regarded runoff as the most important factor with regard to contamination of surface waters in arid areas such as in the Western Cape of South Africa.

The quantity of pesticides, which enters surface waters via runoff, are dependent on a number of factors, and include the time interval between the application of

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pesticides and the first heavy rainfall event. The slope and soil types of the catchments, the quantity of applied pesticide, the chemical nature of the pesticide and the size and characteristics are many factors of buffer-strips [15-16]. Studies have shown that the first heavy rainfall after application results in the highest quantity of pesticides in surface waters [17]. Thus, in the context of the Western Cape, a very important period about determining runoff-related contamination is at the beginning of April, when the first heavy rains normally fall after the end of the spraying season in late February.

The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical-chemical and biological methods. Ionizing radiation degrades aromatic organic compounds, generating substances that are easily biodegraded [18]. Radiation methods for purification and disinfection of wastewater was being developed widely [19]. The most important processes are the combination of ozone and electron beam and ozone treatment [20-21].

2 Experimental Sections

Pesticides Sample solutions were made up by extraction the pesticides from the wastewater by n-hexane. Other organic solvents were used such as toluene and acetone, but the 93% of pesticides was extracted by n-hexane.

The gamma irradiation of sample solutions was conducted using ^{60}Co - gamma cell, Issledovatel – 10 kCi, at a dose rate of 2.5 kGy/h. The dose and dose rates were determined by means of a modified Fricke dosimeter [22]. Samples were irradiated at 20 ^{o}C with doses ranging from 0 to 25 kGy.

The determination of chloride ion, in the irradiated samples, was performed using a Frequency Dosimeter System (FDS).

Qualitative and quantitative analysis of the organic products was performed using UV/Vis Spectrophotometry (Shimadzu UV-Vis, A-120) and HPLC (Bio-Rad- AS-96C) with a ODS-2 (4.6 x 250 mm, 0.9µl , 45 ^{o}C , 95 kg/cm^3) column. The mobile phase used was CH_3CN/H_2O, 65/35, v/v, according to studies of chlorophenols [23]. The HPLC was equipped with a multiple wavelength UV-detector (Shimadzu-SPD-10AV, UV/Vis). GC-mass (Shimadzu-QP5050 A) was used is linked with OPTIMA 5-Accent column and N_2 gas as mobile phase. The Electron impact as detector was used. The individual compounds were detected by measuring their absorption in the wavelength range 200-450 nm, depending on the compounds. The water and eluents for the HPLC were degassed using ultrasound.

The irradiation of samples was conducted using a 10 mL sample placed in sealed glass tube. Selected irradiations were performed in open glass tube in order to study the effect of oxygen on the radiation-degradation.

3 Results and Discussion

The overall objective for controlling chemical pollution is to reduce the toxicity of the compounds prior to discharge to the environment.

The release of choler as a function of gamma dose from the DDT was showed in figure 1.

It can be shown that the DDT transfer to TDE then DDMS by releases of choler then degrade by oxidization to carboxyl group compounds.

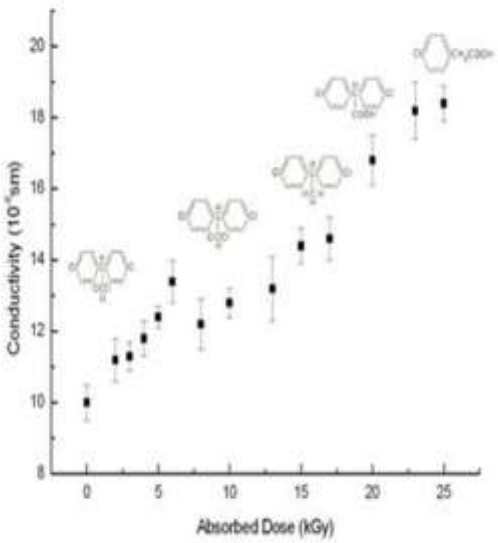

Fig.1. The releases of choler as a function of gamma dose

The release of choler in form of HCl as a function of gamma dose from the DDT was showed in figure2. It can be shown that the DDT transfer to DDD then to DDMU by releases of elimination of HCl then degrade by oxidization to carboxyl group compounds.

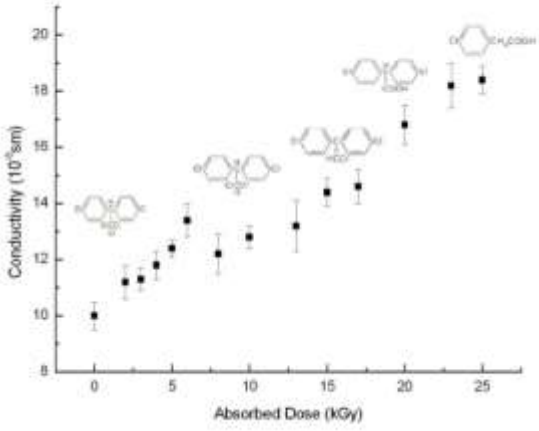

Fig.2: The releases of choler as a function of gamma dose.

A mechanism (Figure3) was suggested to explain the

degradation of DDT if it decomposed to DDD and (Figure4) if it decomposed to DDE. These suggestions were adopted by the remarks reported before [24 - 25]. The final products were determined by comparing HPLC elution times and UV spectra of irradiated solutions with the standard spectra.

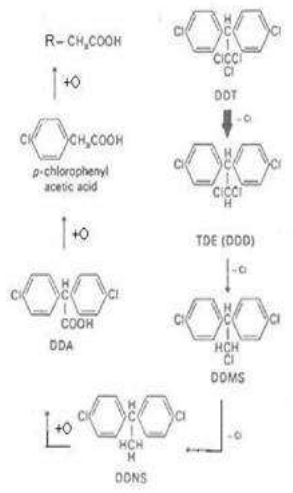

Fig.3: The suggestion of the DDT radiation degradation mechanism.

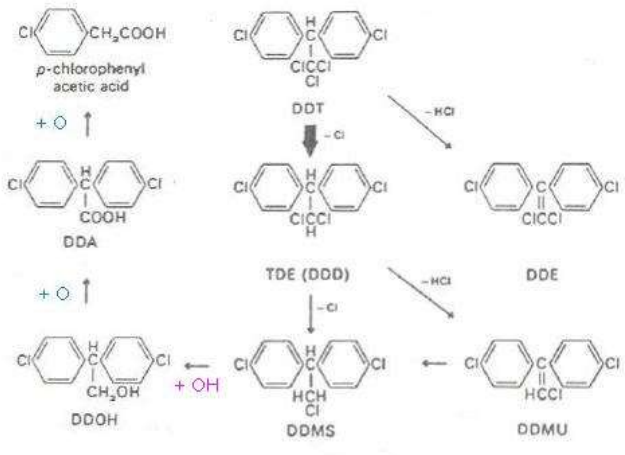

Fig.4: The suggestion of the DDT-DDE radiation degradation mechanism.

The radiation degradation of DDT as a function of gamma dose is shown in figure 5. It can be see the variation on the rate of the degradation pick at 5 to 10 kGy then rapid degradation rate to 25 kGy. These changes may be due to the competition between DDD and DDE when the DDT starts to be decomposed.

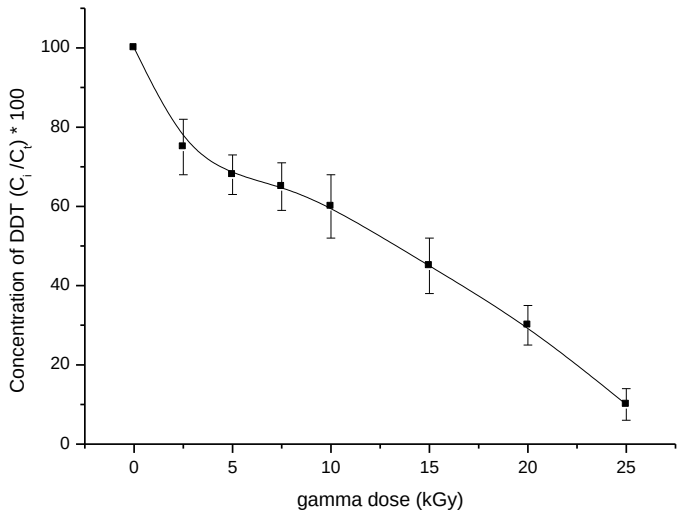

Fig. 5. The variation of the DDT concentration as a function of gamma dose irradiation.

The radiation degradation parameters of DDT and DDE have been calculated on differences mathematical equations to describe the metabolism of insecticides by reductive systems corresponding to suggested mechanisms [26] . The table 1 shows the parameters of DDT and DDE.

Pesticides	k(s^{-1})	Accuracy fitting (%)
DDT	$1.20796 * 10^{-3}$	95
DDE	$0.95024 * 10^{-3}$	97

The radiation formation parameters of carboxyl group resulted from the degradation of DDT and DDE shows in table 2.

Carboxyl group	k(s^{-1})	Accuracy fitting (%)
Phenyl-COOH	$2.4589 * 10^{4}$	94
R-COOH	$1.7895 * 10^{5}$	96

4 Conclusions

The gamma radiation degradation of 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT), and 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE) dissolved in n-hexane was studied. DDT and DDE produced DDD and 2,2-bis(4-chlorophenyl) chloroethylene (DDMU) respectively. The degradation of these two former compounds was larger in iso-octane than in n-hexane or acetone. DDD, DDE and many DDMU would degrades to carboxyl group at 25 KGy.

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