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TEACHING STRATEGY CONCERNING RELATIONSHIP STRUCTURE–BIODEGRADABILITY OF AGRO-ECOSYSTEMS SPECIFIC POLLUTANTS

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abstract: The general plan of the lesson based on classical presentation, dedicated to correlation of the structure with biodegradability of specific agro-ecosystems pollutants was realised. This teaching strategy is projected for third year students at the Environmental Chemistry section which follow the compulsory course: Relationships Structure-Properties–Toxicity of Industrial Pollutants.

key words: structural parameters, biodegradability, toxicity, pesticides, detergents, polymers

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General considerations

Knowledge and applications of efficient cleaning procedures for water, air and soil is a principal objective of current projects, axed on protection of the environment [1].

Artificial biological purification of waste-waters corresponding to aerobic and anaerobic degradation of organic pollutants under influence of bacteria (as bio-mass) adsorbed on filter was in practice in England before 1910 [2].Understanding of relationship between bio-mass composition, rate of degradation, exploit parameters of the bio-filters installation and capacity of biodegradation specific to divers classes of pollutants is not yet exhaustive understood for all synthesis products [3].

Because education for environmental protection is very important in needed change of future technologies in this paper we propose a teaching strategy at university level to show the *dependence between chemical structure and biodegradability for principal class of products used in modern agriculture: pesticides, detergents, synthetic polymers.* These by accumulation can irremediably alter the agro-ecosystems.

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This theme can be integrated in the content of course: **Relationships Structure-Properties-Toxicity of Industrial Pollutants**. This course is compulsory for bachelor in Environmental Chemistry section and is positioned in the third year of study, fifth semester.

The **instructive-formative scope** of proposed study follow to introduce, explain and apply the polls notions: *chemical structure*, *biodegradability* to nominated classes of agro-ecosystems pollutants.

The **educational scope** consists in development of the *discerning capacity* and *selective thinking* of students.

The proposed theme can be presented by classical presentation and dialogue as follows: *Introduction*.

Concept of chemical structure supposes a complex interaction between molecules constituents' atoms, determining some specific properties for two substances for example, which posses the same chemical composition and molecular weight – as **A.M. Butlerov** in 1864 introduced this notion [2].

Development of the lesson

The modern studies of molecular structure are concretised by determination of *geometrical parameters* (bond lengths between component atoms, angles between these lengths, spatial form of molecule) and *energetic parameters* (length strength, deformability/polarisability of molecule, its behaviour in magnetic field, distribution of electric charge/density) by modern methods of structural analysis [4]

Notion of *biological degradability* or *biodegradation* is also analysed in literature [5,6]. By this term is understood sum of physical chemical and biochemical processes for transformation of substance by micro-organisms. Process of degradation is in essence a mineralization and it is the key of reduction stage in the recycling of the elements [7].

Beyjerik [5] considered that bacteria present an infaibility concerning mineralization of organic natural compounds. *Resistance at biodegradation* of synthetic products (when time of degradation corresponds to months and years) is described in ecological terms in two undesired effects:

Immobilization of vital elements, contained in pollutants, in an inassimilable form by plants

Accumulation of toxic products

Exists some types of biodegradation appreciated after criteria which consider *structural, kinetic* and *ecological characteristics* of pollutants [2].

Essentially, when successive changes supported by substances lead to disappearance of undesired properties from ecological point of view, and substance is not completely converted in inorganic compounds it is a *apparent* biodegradation; when mineralization is attained ,we have an *total* or *intrinsic* biodegradation [8].Very much decisions for substance introduction in fabrication are based on concept of apparent biodegradation(these decisions are based on the determined values of threshold of biodegradation, rate and probability of biodegradation [3]). These lead to diversification of unhappy actions concerning man and environment, associated with undesired effects. Advantageous decisions on log term for substance introduction in fabrication must be argued on total biodegradability values [3,9].

Analysis of structural characteristics for compounds from organic pesticides class (*i.e.* organic substances destined for inhibition or destruction of the different life forms) and of its persistence in agro-ecosystems values probed a high soil remanence for chlorinated derivatives. For example, the case of DDT: synthesized in 1874, used as insecticide from 1939, in present interdicted in developed countries due to its accumulation in lipid tissues of mammals (s. Table 1).

Table 1 Structure-biological activity correlation for different pesticides.

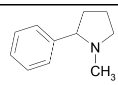
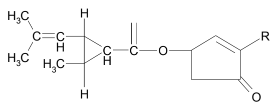
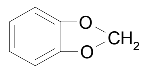
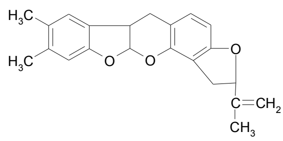
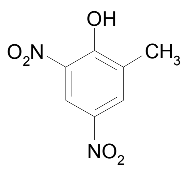
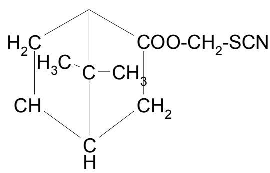
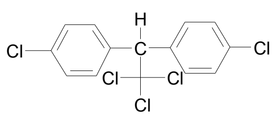
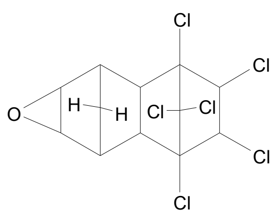
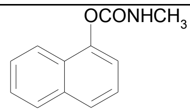
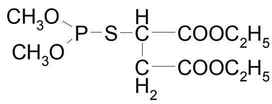
No	Class	Representative compound	Structural formula	Observations
1	nicotinoids	nicotine		–
2	piretroids	piretrine I		low toxicity at metabolisation. It is used with synergic additive like: 
3	rotenoids	rotenone		-
4	dinitrophenols	DNOC		wide spectrum of bactericide activity
5	organic thiocianids	Thamit		–
6	chlorinated hydrocarbons (DDT and analogues)	DDT		long persistence:2-5 years; accumulates in the lipoid tissue
7	cyclodienes	Dieldrin		wide spectrum of bactericide activity accumulates in mammal tissues concentrating 22 times

Table 1 *Continued.*

No	Class	Representative compound	Structural formula	Observations
8	carbamates	Carbaryl		–
9	organic compounds with P and S	malathion		big toxicity for mammals (more reduced at the derivative with $(CH_3)_2$.) It is rapidly metabolised in the mammals liver

For pesticides class was tested a relation describing biological activity based on substituent constant and regression analysis introduced by Hansch theory [10]. This evidenced that influence of substituent on basic molecule can be characterised by three effects: *electronic*, *steric* and *hydrofobic*.

$$\text{Log}(1/\text{C}) = -k_1\Pi^2 + k_2\Pi + k_3\,\sigma + k_4\,\text{E}_\text{S} + k_5 \qquad (1)$$

Where: C – molar concentration of substance; $k_1 \div k_5$ – rate constants reactions for substances in organism; Π – hydrophobicity constants of substituent defined as difference between logarithms of partition coefficient between octanol/water of substituted and unsubstituted compounds; E_S – steric Taft constant; σ – substituent Hammet constant which reflects influence of conjugation and electronic effects on rate constant.

To halogenated pesticides rate of bacterial degradation is dependent on number, position and type of halogen substituent. For example, in case of phenoxy acetic acids substitution with chlorine in *para*-position determine maximal lability of molecule and substitution in *ortho* inhibes degradation [11]. First effect depasses in significant measure the second.

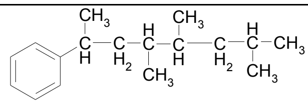
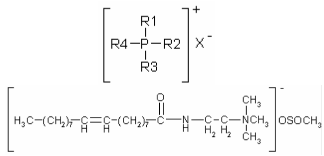
In [12] are resumed generalizations concerning relationships between structure of detergents and its biodegradability (see Table 2).

Table 2 Relation persistence-initial process of degradation in different pesticides.

No	Representative compounds	Persistence in soil	Type of initial degradation process
1	Organophosphates	1-12 weeks	ester hydrolysis
2	Carbamates	2-9 weeks	ester hydrolisis
3	Halogenated aliphatic acids	3-10 weeks	dehalogenation
4	Phenoxyacids	4 months	reduction
5	Triazines	3-12 months	dealkylation or dehalogenation
6	Chlorurated hidrocarbons	2-5 years	dehydrohalogenation or epoxidation

Biodegradability is favoured by linearity of hydrophobic components and disfavoured by its ramification, particularly by presence of terminal quaternary carbons. It is observed that the type of hydrophilic group have a minor influence in the biodegradability. *Principle of the* *distance* applied to alkylbenzensulphonic type detergents indicate that raised distance between sulphonic and the extremity of the hydrophobic group increase rate of primary biodegradation. In the case of 4 classes of detergents (anionic, cationic, ampholitic and nonionic) (see table 3) may consider presence of apparent degradation at anionic detergents and satisfactory capacity of degradation to nonionic detergents.

Table 3 Classification of detergents.

No	Class of detergents	Subclass	Examples	Observations
1	anionic detergents	-oils and sulphatated fats -condensed products of fatty acids -bibasic acids derivatives (succinic, phtalic)		high production until 1966. intense
2	cationic detergents	amines sulphonium salts phosphonium salts ammonium salts		applications in textile industry for impermeable. Bactericide activity
3	ampholitic detergents	polypeptides betaine type products sulphobetaine type products		–
4	non-ionic detergents	esters of fatty acids with alcohols and poly alcohols	$CH_3(CH_2)_{11}-O-(CH_2CH_2\text{-}O)_{12}-OH$ $CH_3(CH_2)_{10}-COO-(CH_2\text{-}CH_2O)_9H$	–

Biodegradation properties of synthetic polymers are investigated in parallel with theirs increased utilisation. Until 1939 researchers considered their resistance to microbial attack. Significant alteration of the objects realized from these materials in tropical regions have been observed in the time of the second World War [7] when the conjugated effects of O_2,UV radiation, water environment and biological factors have been observed.

Polymers resistance to biodegradation is due to following structural factors or its combinations:

- molecular structure in which the principal catenas contain carbon-carbon bonds characterized by high dissociation energies
- small solubility in water and lipids molecular weights (10^4-10^7 Daltons)
- high branched structure

Environmental problems are caused by polymers of used anvelops, containers, ambalages polymer based.

For containers and ambalages is necessary design of the materials with significant biodegradation or regular collection of unbiodegradable ones. Starting from observations of high rate of plastifiants biodegradation have been realized polyethylene containers (non biodegradable polymer) which disappear in atmospheric conditions after 2 weeks because in process of polymer fabrication are added substances containing carbonyl groups which modify the photochemical properties of polymer. The break of carbon-carbon bonds neighboured with carbonyl group is realized by a Norrish process [7].

Conclusions

We proposed a teaching strategy for the correlation between understanding of molecular structure of pollutants in relation with biology and repartition in hydro and biosphere, of the rate and susceptibility for biodegradation. This is interesting for knowledge of short and long-term effects of pollutants on the environment.

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