



FAO European Cooperative
Research Network



Recycling of Agricultural, Municipal and Industrial Residues in Agriculture

Network Coordinator: José Martinez, Cemagref, Rennes (France)

RAMIRAN 2002

**Proceedings of the 10th International Conference
of the RAMIRAN Network**

General Theme: Hygiene Safety

**Štrbské Pleso, High Tatras, Slovak Republic
May 14 - 18, 2002**

Edited by Ján Venglovský and Gertruda Gréserová

ISBN 80-88985-68-4



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ELECTROLYTIC TREATMENT OF OBSOLETE PESTICIDES (METHYL-PARATHION CASES)

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ABSTRACT

The problem of disposal of obsolete and unwanted pesticides stocks is widespread and remains extremely serious and urgent. Many such stocks have seriously deteriorated and are currently a source of severe pollution, a threat to human health, the environment and development in general. The preferred way to dispose of obsolete pesticide is high-temperature incineration.

This paper report on the detoxification of organophosphoric pesticides, using an electrolytic system in a laboratory pilot plant scale. Commercial Methyl-Parathion was treated by an electrochemical method using Ti/Pt as anode and Stainless Steel 304 as cathode. Sodium chloride was added as an electrolyte and the mixture was passed through an electrolytic cell for a total time 2 h. Due to the strong oxidizing potential of the chemical produced, the organic pollutants were wet oxidized to carbon dioxide and water.

With the use of the above method, the achieved destruction of COD was over 85%. The mean energy consumption was 2 to 3.5 kWh per Kg⁻¹CODreduction. The COD / BOD₅ ratio decreased during electrolysis from 5.2 to 2.0. This decrement indicates that electrolysis could be detoxificate this pesticide, and then, lead them to a biological treatment.

INTRODUCTION

Commercial synthetic chemical pesticides are traded in every country and reach even the remotest regions. Wherever pesticides are used, unusable or unwanted pesticides and empty pesticides containers have to be managed and disposal of safely. Most of the pesticide stocks are kept in substandard stores, which lack impermeable floors having little or no ventilation. It is not uncommon for drums to be stored in the open, exposed to direct sunlight and rain. Often stores are located in urban areas or near bodies of water, such as rivers, irrigation schemes or ports. As time goes by, containers deteriorate and start leaking. Unfavorable climatic conditions and high temperatures inside poorly ventilated stores accelerate this process. High temperatures also increase the pressure inside drums, which increases the chance of leakage. Sometimes containers have not been designed for tropical conditions and start leaking soon after arrival. The result is that many stores are heavily contaminated with leaked pesticides [1,2,3].

High-temperature incineration in dedicated hazardous waste incinerators is the currently recommended method for disposal of obsolete pesticides. But such sophisticated incinerators do not exist in developing countries. It is therefor necessary to re-package pesticide waste in new approved containers where they exist in developing countries, transport them by sea to a country where there is dedicated hazardous waste destruction facilities. So far obsolete pesticide waste has been shipped to Europe. FAO estimates the

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cost of disposal range between US\$ 3000 and US\$ 4500 per tonne depending on a number of factor [2]. On the basis of global estimates totaling 250000 tonnes of obsolete pesticides, about \$1.25 billion would be needed to destroy all stocks.

Various innovative technologies were proposed for disposal of obsolete pesticides. These technologies include the photocatalytic oxidation [4,5], ultrasonic radiation [6], bioremediation, thermal disruption etc. The major disadvantage is these technologies designed to remediation relatively low levels of specific contaminants from environmental media such as air and groundwater, rather than high concentration of obsolete pesticides stocks.

In recent years there has been increasing interest in the use of electrochemical methods for the treatment of recalcitrant toxic wastes [7,8,9,10]. The organic and toxic pollutants present in such wastes, like phenols which are present in many pesticides, are usually destroyed by an anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone etc. [8,9,10]. Electrochemical methods have been successfully applied in the purification of domestic sewage [11], landfill leachate [12], tannery wastes [13], olive oil wastewaters [10], textile wastes [14] etc. These methods are environmentally friendly and they do not form new toxic wastes.

The electrochemical reactions, which take place during the electrolysis of a brine solution, are complicated and not entirely known. For the time being only assumptions can be made, based on the oxidation products produced during electrolysis that can be determined (i.e.; Cl_2 , ClO_2 , O_3 , $\text{OH}\cdot$, $\text{O}\cdot$, $\text{ClOH}\cdot$, H_2O_2 , O_2 , H_2 , CO_2). The radicals $\text{OH}\cdot$, $\text{O}\cdot$ and $\text{ClOH}\cdot$ have a very short life due to their high oxidation potential and are either decomposed to other oxidants (such as Cl_2 , O_2 , ClO_2 , O_3 , and H_2O_2) or oxidise organic compounds (i.e., direct oxidation). The primary (Cl_2 , O_2) and secondary (ClO_2 , O_3 , and H_2O_2) oxidants that are produced from the destruction of radicals have quite a long life and are diffused into the area away from the electrodes, thus continuing the oxidation process (indirect oxidation). Nevertheless the main oxidate active, is this of direct oxidation (that take place in a close area around the electrode) than the indirect oxidation.

This paper deals with the treated a commercial organophosphoric pesticide (methyl-Parathion) by an electrochemical method, using Ti/Pt electrode.

MATERIALS AND METHODS

The Laboratory Pilot Plant For The Electrolysis

The experimental plant is shown in Figure 1. The electrolytic cell was a vessel of activated volume 6 L. An Ti/Pt electrode was used as anode. Its dimensions were 14 cm in length and 1.5 cm in diameter. The electrode lied to a perforated stainless steel cylinder served as cathode. This construction ensured homogenous dynamic lines between anode and cathode. The system was cooled down by a heat exchanger. The electrodes were operated at 30 and 36 Amperes D.C.

Aqueous solutions 25 percent (v/w) of methyl Parathion were used. Sodium Chloride 2 and 4 % (w/v) was added as an electrolyte and 0.6% (w/v) Ferrous sulfate (FeSO_4) as

an oxidant.. The mixture was added in the electrolytic cell with a centrifugal pump with a flow rate of 3 ml/min. The total time of electrolysis was 2h.

In order to examine how the waste was detoxified the COD and BOD₅ was measured, according to the Standard Methods for Examination of Water and Wastewater, [12] while for the statistical analysis three analyses were carried out.

RESULTS

As it is observed from Table 1, the application of electrolysis methyl-Parathion has the ability to reduce the COD in satisfactory levels. The per cent reduction was over to 90%. This is in agreement with previous studies of other researchers, which used electrolysis at different waste [11,14,15,16].

Table 1. Reduction of COD, ΔT and pH after 2h electrolysis of methyl Parathion.

NaCl %	A	Input COD mg/L	Output COD mg/L	% COD Reduced	Energy Consumption kWh	$\Delta T^{\circ}C$	pH
2	30	77810	5923	92,39	0,990	37,5	3,49
2	36	68440	6865	89,97	1,266	43,7	3,12
4	30	70603	6931	90,18	0,783	31,1	3,35
4	36	76569	5009	93,46	0,948	25,0	3,28

Table 1 shows the change of pH in brine solution during electrolysis. In all cases the pH became quickly acid (pH = 3.2). It is obvious that the continuous addition of high levels of organic matter in the electrolytic cell, resulted in the drop of pH and a strong acid solution

Table 2. Energy Consumption for the reduction 1Kg of organic matter. (KWh / Kg COD rem.)

	2% NaCl	4% NaCl
30 A	2,295	2,048
36 A	3,427	2,208

The efficiency of the electrolysis system depends on the energy consumption for the reduction of 1Kg COD of organic matter, which is one of the most important factors in the economics of electrolysis. It is obvious that a lower ratio kWh / Kg CODr was desirable. In all cases the respective ratio was varied at low levels (2.0 to 3.4 kWh per Kg COD reduced). Table 2 shows that the doubling of percentage of NaCl (from 2% to 4%) improved the corresponding ratio by about 35% (at 36A). Furthermore the increase of electric current from 30A to 36A worsen the corresponding ratio. The best results obtained from electric current 30A and NaCl concentration 4%.

Table 3 shows the change of BOD₅ of methyl-Parathion (4% NaCl - 30A), when they degraded using electrolysis. The initial ratio COD / BOD₅ was very high (5.25). These high values indicate that this pesticide have high toxicity and none biological method for its degradation can be applied. After electrolysis the respective ratio was sensibly lower (2.03). This means that the final product was detoxified and a biological method can be applied.

Table 3. Change of BOD₅ of methyl-Parathion solution after 2h electrolysis (30A- 4% NaCl)

Input	Output	%	Initial	End
BOD ₅ (mg)	BOD ₅ (mg)	Reduction	COD / BOD ₅	COD / BOD ₅
83046	23651	71,52	5,25	2,03

CONCLUSIONS

For the above results we can conclude that we can destroy the obsolete organophosphoric pesticides stock by the electrolytic oxidation. We achieve high degradation of entered COD. In all cases the effectiveness of the electrolysis system was in high levels. The ratio kWh / CODreduction is one of the most important factors in the economics of electrolysis. In the present study this ratio was found to be low that verify the ability of electrolysis. This low value indicates that this method for the treatment of pesticides obsolete stockpiles, require low energy consumption, comparable to the energy consumption require to any biological system.

The decrease of COD / BOD₅ ratio indicate that the initial toxic pesticides solution was detoxified in high levels and a biological method can be applied.

From these results it seems that electrolysis could be a feasible method for the obsolete pesticide stockpiles treatments, rapid, with low operating cost.

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