



Electrochemical treatment of methyl parathion based on the implementation of a factorial design

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Abstract

Commercial methyl parathion was treated by an electrochemical method using Ti/Pt as anode, Stainless Steel 304 as cathode and sodium chloride as electrolyte. Based on a number of preliminary experiments, a factorial experimental procedure was designed in order to optimize the electrolysis efficiency, in terms of % removed COD and energy consumed kW h per kg of removed COD. The parameters examined were the temperature, the stirring rate of the brine solution, the input rate of the organic material, the current density, the electrolyte concentration and the concentration of Fe²⁺ ions added. In the experimental range studied, the lower energy consumption measured was 6.61 kW h (kg COD_r)⁻¹ and the higher % COD reduction measured was 86.3%. From a mathematical model, the optimum conditions for the electrochemical treatment of MeP for 2.03 kW h (kg COD_r)⁻¹ were found to be: Input rate of MeP 4300 mg COD min⁻¹, NaCl concentration 4.5%, 4 g l⁻¹ of added FeSO₄, current density 0.47 A cm⁻², temperature 45 °C and stirring rate 400 rpm. An experiment was conducted under these optimum conditions which resulted in a satisfactory removal of the organic load (in terms of COD, BOD₅). Furthermore, a significant improvement in the COD/BOD₅ ratio was achieved, rendering the effluent amenable to further biological treatment.

1. Introduction

In many countries, large quantities of pesticides have accumulated since they have lost their desirable characteristics. Although these products are not suitable for use, they still contain toxic compounds. Many surplus pesticides, still within their expiry limits, may become useless, when their future use is prohibited due to toxicological or environmental concerns. Food and Agricultural Organization of the United Nations (FAO) estimates that more than 400 000 tonnes of obsolete pesticides are stocked worldwide [1].

The biological degradation of pesticides is difficult due to their high toxic content [2, 3]. An ideal treatment method for pesticides should be non-selective, should achieve rapid and complete degradation to inorganic products, and should be suitable for small amounts [4, 5]. Today the main disposal method for obsolete pesticide stocks is incineration, an impractical and expensive procedure [1]. FAO estimates that the cost of such disposal ranges between 3000 and 4500 US\$ per tonne, depending on a number of factors [1].

Methyl parathion (IUPAC: *O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate) is a widely used organophos-

phoric pesticide for crop production and fruit tree treatment. It is a very toxic substance to all organisms and is graded in the first toxicity category according to the US Environmental Protection Agency (EPA): High risk for health EPA I. The acute oral LD₅₀ for rats is approximately 6 mg kg⁻¹ and for male mice 24 mg kg⁻¹. The acceptable daily human intake is 0.02 mg kg⁻¹ body weight [6], and the acceptable concentration in ground water for the European Union is 0.1 µg l⁻¹.

Various innovative technologies have been proposed for methyl-parathion treatment. This includes the use of UV and hydrogen peroxide [7, 8], ultrasonic radiation [9] or mercury-promoted hydrolysis [10]. The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with a very low active ingredient content and are not suitable for the higher concentrations of unwanted pesticides.

1.1. Electrochemical oxidation – theoretical approach

Recently, there has been an increasing interest in the use of electrochemical methods for the treatment of

recalcitrant toxic wastes [11–14]. The organic and toxic pollutants present in such wastes, such as phenols (a popular pesticide ingredient), are usually destroyed via production of oxidants such as hydroxyl radicals, ozone etc. [11–14]. These methods are environmentally friendly and do not produce new toxic wastes. Electrochemical methods have been successfully applied in the purification of domestic sewage [15, 16], landfill leachate [17], tannery wastes [18], olive oil wastewaters [19, 20], textile wastes [21], etc.

This paper deals with the treatment of a commercial MeP formulation by an electrochemical method in a laboratory scale plant using Ti/Pt as anode, Stainless Steel 304 as cathode and sodium chloride as electrolyte. The purpose of this study was to identify the main parameters influencing the performance of an electrochemical oxidation system and to achieve an effective degradation of methyl parathion.

2. Materials and methods

2.1. Laboratory scale pilot plant

The experimental plant is shown in Figure 1. The electrolytic cell was a cylindrical vessel (V), which contained 6 l of different concentrations of brine solution ($\text{H}_2\text{O} + \text{NaCl}$). A Ti/Pt cylindrical electrode (14 cm long \times 1.5 cm diameter) was used as anode. It was covered by platinum alloy foil approximately 0.22 mm thick. The electrode was located inside a perforated stainless steel 304 cylinder (14 cm long \times 8 cm diameter) which served as cathode. This construction ensured homogenous dynamic lines between anode and cathode and provided good contact of the waste with the electrode.

In all cases, to mix the brine solution and ensure the continuous presence of untreated organic matter close to the anode, an agitator was used in the cell. The aqueous solution of methyl parathion was added to the cell continuously using a peristaltic pump. Electrolysis was carried out until effluent COD was maintained constant. Every 15 min, a sample was collected from the cell for analysis. Three experiments were performed under the same conditions and the results presented are the mean values. In all cases, the pH was kept constant in the range 2.5–2.8.

2.2. Raw material

The commercial formulation Folidol M (40% w/v methyl parathion) was purchased from Bayer.

2.3. Methodology

2.3.1. Factorial experimental procedure

The aim of the experimental procedure was to determine the influence of some basic process parameters on the efficiency of the electrochemical treatment in terms of % COD removed and energy consumed as $\text{kWh} (\text{kg COD}_r)^{-1}$ (optimization parameters). The parameters that generally influence the performance of an electrochemical oxidation system are temperature ($^\circ\text{C}$), stirring rate (rpm) of the brine solution, feed rate (mg COD min^{-1}), current density (A cm^{-2}) and electrolyte concentration (% NaCl w/v) [22]. It has also been reported that the addition of Fe^{2+} ions ($\text{g FeSO}_4 \cdot 7\text{H}_2\text{O l}^{-1}$) plays a favorable role through indirect generation of hydroxyl radicals from mild oxidants such as oxygen, ozone, hydrogen peroxide etc. (Fenton's reactions), which are byproducts of an electrolytic oxidation procedure (A.G. Vlyssides, submitted for publication).

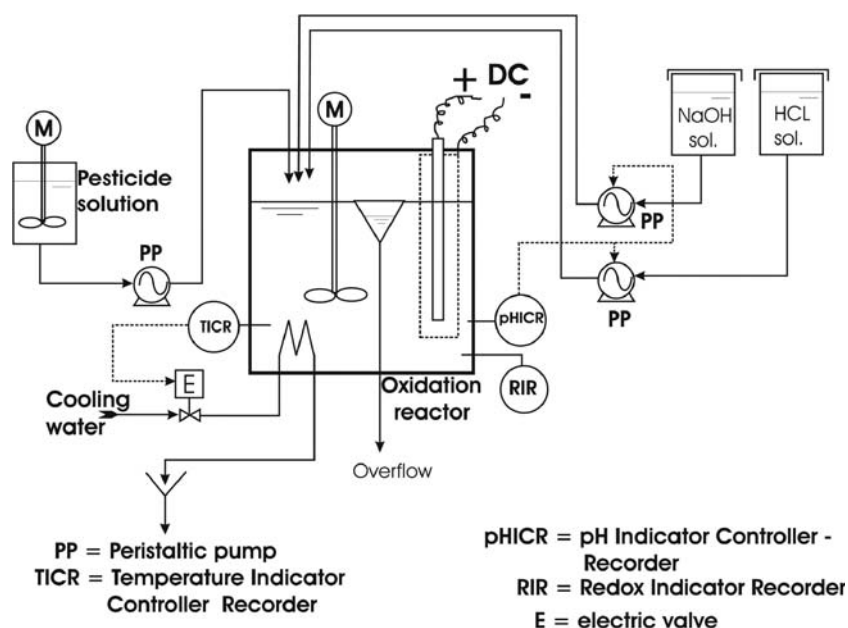


Fig. 1. The Laboratory Scale Pilot Plant.

These parameters are referred to as ‘controlling parameters’ of the system.

The effect of the controlling parameters on each optimization parameter was estimated by performing a 2^6 factorial experiment. In general, by using a 2^n factorial design, n controlling parameters interrelate to an optimization parameter through an appropriate linear model. Their significance can also be estimated and assessed [23, 24]. Then the most significant variables are altered stepwise, aiming at the determination of the optimal experimental conditions. The levels of the controlling parameters are given in Table 1. The experimental area of the factorial design was pre-determined in preliminary trials.

In the 2^6 factorial design, 64 experiments were carried out. Five extra experiments in the center of the design (level 0) were also conducted for statistical purposes. From these data, a mathematical model was constructed whose adequacy was checked by the Fisher criterion. According to the latter, the following ratio should follow the F -distribution with level of importance $p = 5\%$:

$$F_{\text{exp}} = \frac{\zeta_{\text{ad}}^2}{\zeta_Y^2},$$

where $\zeta^2(Y)$ is the standard deviation and ζ_{ad}^2 , the adequacy deviation and is calculated by the following equation:

$$\zeta_{\text{ad}}^2 = \frac{\sum_{i=1}^N (Y_i - \hat{Y}_i)^2}{df}$$

where Y_i is the experimental i value; \hat{Y}_i , the estimated i value from the model determined; df , the number of degrees of freedom; N , the number of trials.

As far as the determination of statistically important parameters is concerned, the procedure described below was followed. The coefficient deviation is defined as:

$$\zeta^2(b_j) = \frac{\zeta_Y^2}{N}$$

The importance of the coefficient is checked by:

$$t = \frac{|b_j|}{\zeta(b_j)}$$

Table 1. Controlling parameters and their levels at the factorial experiment

Controlling parameters	Variation intervals			
		-1 Level	0 Level	+1 Level
FeSO ₄ · 7H ₂ O (g l ⁻¹)	X ₁	0	4	8
NaCl (% w/v)	X ₂	1	2	3
Influent mass rate (mg COD min ⁻¹)	X ₃	1200	1800	2400
Current density (A cm ⁻²)	X ₄	0.43	0.47	0.51
Temperature (°C)	X ₅	30	45	60
Stirring rate (rpm)	X ₆	200	400	600

where t should follow the Student distribution for importance level $p = 0.05$ and degrees of freedom those of the deviation $\zeta^2(Y)$.

After the mathematical model construction and the determination of statistically important parameters, an effort to find the optimum conditions for the efficiency of the electrochemical treatment of MeP was made. This was performed through a steepest ascent method [23].

2.3.2. Methods of analysis

The chemical oxygen demand (COD) and the biochemical oxygen demand (BOD₅) were measured, according to the Standard Methods for Examination of Water and Wastewater [25].

3. Results and discussion

The energy consumption is one of the most important factors in the cost of electrolysis and a low ratio of kW h (kg COD_r)⁻¹ is desirable. According to the results of the factorial experiments and by following a specific analytical procedure [24, 25], the following linear model was estimated, interrelating the ratio of kW h (kg COD_r)⁻¹ (Y_1) with the selected controlling parameters of the system:

$$Y_1 = 10.31 - 0.23X_1 - 1.41X_2 - 2.78X_3 + 0.51X_4 - 0.05X_5 + 0.04X_6 + 0.32X_1X_2 + 0.79X_2X_3$$

Adequacy of the model: $F_{\text{exp}} = 4.32 < F_{\text{tab}} = 8.57$. The adequacy of the mathematical model derived from the factorial design was checked by the Fisher criterion.

Statistically, the most significant parameters ($p < 0.05$) were the feed rate of MeP, the concentration of NaCl and their interaction. The minus (-) in the above equation indicates that an increase of the input rate of methyl-parathion solution and NaCl concentration leads to a lower kW h (kg COD_r)⁻¹ ratio and, consequently, to a more effective electrolysis. In addition, the applied current was a significant parameter, although it is worth noting that the concentration of NaCl was nine times more significant in magnitude, the feed rate of MeP solution 30 times and their interaction 2.5 times. The influence of the other controlling parameters was not significant. It was shown through statistical analysis that the interactions between three or more parameters were negligible.

In the experimental range studied, the lower energy consumption measured was 6.61 kW h (kg COD_r)⁻¹ in the experimental point ($X_1, X_2, X_3, X_4, X_5, X_6$) = (8, 1, 2400, 0.43, 60, 600).

According to the results of the factorial experiments, the following linear model was estimated, correlating the % COD_r (Y_2) with the selected controlling parameters of the system:

$$Y_2 = 78.51 + 1.32X_1 - 0.92X_2 + 1.01X_3 + 3.17X_4 + 0.23X_5 - 0.28X_6 - 1.33X_1X_3 - 2.34X_2X_3$$

The adequacy of the model based on the Fisher criterion was: $F_{exp} = 7.94 < F_{tab} = 8.57$.

As far as % COD removed (Y_2) is concerned, there are no statistically significant parameters ($p < 0.05$). Only the feed rate of methyl-parathion solution was close to the statistical significance level. Thus, the optimum conditions determined by this parameter are in accordance with the fact that in all cases the achieved % COD reduction was high (above 70%). This fact is also confirmed by previous studies, which used electrochemical oxidation for the treatment of various wastes, for example, olive oil wastewater [20], leachate [16], tannery wastes [18] and textile dye wastewaters [21], where the COD removal was 93, 84, 52 and 90%, respectively. In the experimental range studied, the higher % COD reduction measured was 86.3% at the experimental point ($X_1, X_2, X_3, X_4, X_5, X_6$)=(8, 1, 2400, 0.51, 30, 200).

After the statistical analysis of the factorial experiment, optimization of the energy efficiency (Y_1) was performed. For this purpose and by taking as startup point the center of the factorial design, the feed rate of MeP was increased by 200 mg COD min⁻¹ and the NaCl concentration was increased proportionally according to the ratio found in the linear model by the factorial experiment (increasing by 0.2%). Furthermore, according to the linear model and the subsequent parameter interactions, a 200 mg COD min⁻¹ increase in the feed rate of MeP solution should be followed by a negligible increase of 0.00085 A cm⁻² in current density. As a result, in all the experiments aiming at optimizing the experimental conditions, the current density was kept constant and only the other significant parameters were changed.

From Figures 2 and 3, the optimum point (in terms of kWh (kg COD_r)⁻¹ ratio) for the electrochemical treatment of MeP was found to be 2.03 kWh (kg COD_r)⁻¹ for the following experimental conditions: MeP feed rate 4300 mg COD min⁻¹, NaCl concentration 4.5%, 4 g l⁻¹

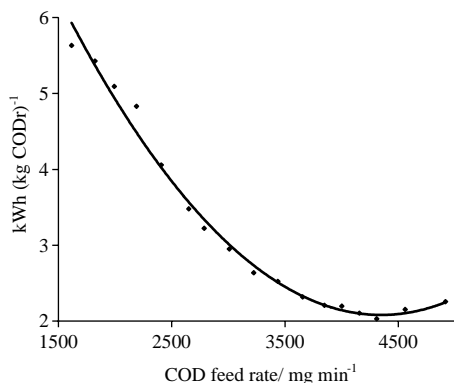


Fig. 2. Relation between kWh (kg COD_r)⁻¹ ratio and input rate of mg COD per min for 4 g l⁻¹ of added FeSO₄, current density 0.47 A cm⁻¹, temperature 45 °C and stirring rate 400 rpm.

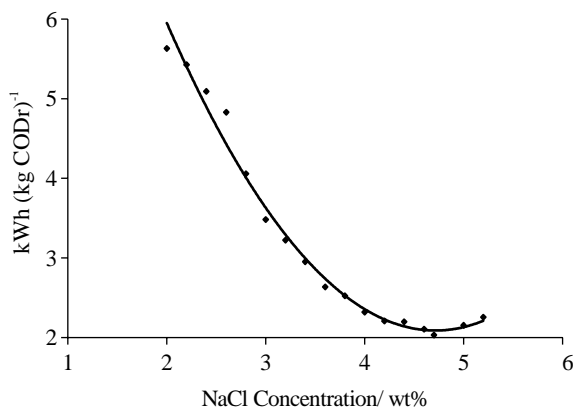


Fig. 3. Relation between kWh (kg COD_r)⁻¹ ratio and sodium chloride concentration for 4 g l⁻¹ of added FeSO₄, current density 0.47 A cm⁻¹, temperature 45 °C and stirring rate 400 rpm.

of added FeSO₄, current density 0.47 A cm⁻¹, temperature 45 °C and stirring rate 400 rpm.

At this point an overall experiment was performed and the achieved % COD and BOD₅ reduction, the COD/BOD₅ ratio and the pH were measured. These results are presented in Figure 4.

After 2 h of electrolysis, 80 and 50% removal of the COD and BOD₅, respectively, was achieved. The input and output for COD were 498 267 and 102 992 mg l⁻¹, while the input and output for BOD₅ were 101 719 and 50 735 mg l⁻¹, respectively.

The COD/BOD₅ ratio indicates the relative degradability of a waste. A low COD/BOD₅ ratio implies a large biodegradable fraction. In contrast, a waste with a high COD/BOD₅ ratio has a large non-biodegradable fraction [25]. The use of the COD/BOD₅ ratio as an indicator of biodegradability is advantageous over the sole BOD₅ measurement, since this ratio also takes into account the extent of the total oxidation that has occurred during electrolysis [26]. A waste with COD/BOD₅ ratio < 2 can be treated using a biological system, whereas a waste with COD/BOD₅ ratio > 5 can be

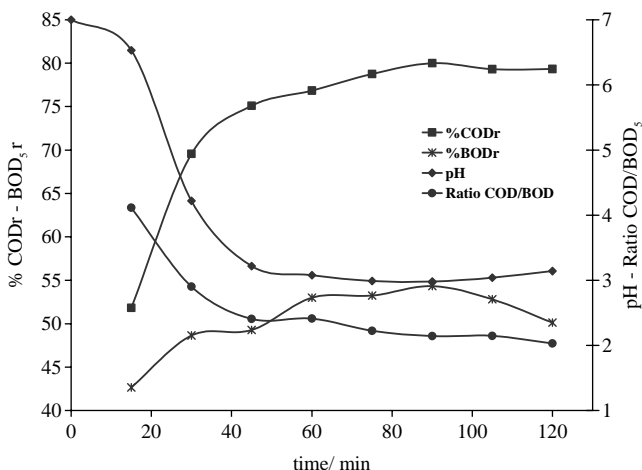


Fig. 4. Change of degradation parameters during MeP treatment in optimal conditions.

considered as toxic [25]. The initial ratio COD/BOD₅ of the 8% MeP mixture was 4.90 while at the end point it was 2.03. This shows that the final product had been detoxified and a further biological treatment could be applied.

4. Conclusions

In this study, methyl parathion was treated by an electrochemical procedure and the results were satisfactory.

The kW h (kg COD_r)⁻¹ ratio, one of the most important factors influencing the cost of electrolysis, was found to be quite low after optimization, where the initial concentration of MeP was found to play a significant role. The higher the initial concentration of MeP the more effective the electrolysis and the lower the kW h (kg COD_r)⁻¹ ratios. The NaCl present in the solution was found to be another important factor for the efficient degradation of MeP. By increasing the NaCl concentration, there was a decrease in the consumed kW h per COD_r.

A high COD degradation was found in all cases. Through the optimization of the % COD reduction, no statistical important parameters were found. Furthermore, a considerable improvement in the biodegradability index (COD/BOD₅) of the treated pesticide was achieved.

Electrochemical oxidation may prove to be a feasible method for the treatment of toxic wastewater with a high concentration of methyl parathion and may also find use as a pretreatment stage before biological treatment.

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