



Detoxification of methyl-parathion pesticide in aqueous solutions by electrochemical oxidation

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Abstract

Commercial methyl-parathion (MeP) was detoxified using an electrochemical method that employed a Ti/Pt anode and stainless steel 304 as cathode. Sodium chloride was added as electrolyte and the mixture was passed through an electrolytic cell for 2 h. Due to the strong oxidizing potential of the produced chemicals, the organic pollutants were wet oxidized to carbon dioxide and water. A number of experiments were run at laboratory scale. Reductions of COD and BOD₅ were both over 80% and the mean energy consumption was 18–8 kWh per kg⁻¹ COD reduced (COD_r). The degradation of MeP was more effective when the pH of the brine solution was in the acid range than when it was in the alkaline range. From the results it can be concluded that electrolysis could be used as an oxidation pre-treatment stage for detoxification of toxic wastes with MeP.

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1. Introduction

Commercial synthetic chemical pesticides are utilized in all countries and as a consequence reach even the remotest regions. Wherever pesticides are used, unusable or unwanted pesticides and empty pesticides containers have to be managed and disposed safely. Food and Agricultural Organization of the United Nations (FAO) estimated that more than 250,000 tonnes of obsolete pesticides are stored worldwide [1].

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High-temperature incineration in dedicated hazardous waste incinerators is the currently recommended method for the treatment of obsolete pesticides. But sophisticated incinerators do not exist in developing countries. It is therefore necessary to repackage pesticide waste in new approved containers in developing countries and transport them by sea to a country where a dedicated hazardous waste destruction facility exists. Normally obsolete pesticide wastes are shipped to Europe. The FAO estimates the cost of disposal range between US\$ 3000 and 4500 per tonnes depending on a number of factors [1,2]. However, many pesticide suppliers and national authorities recommend burying or burning of waste pesticides and empty containers. However, buried chemical waste can contaminate soil and leach into surface or groundwater, while burning pesticides and containers release highly toxic fumes [3].

Various innovative technologies have been proposed for the disposal of obsolete pesticides. These technologies include photocatalytic oxidation [4,5], ultrasonic radiation [6], bioremediation and thermal desorption [2]. The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with a very low active ingredient content, rather than highly concentrated obsolete pesticides stocks.

In recent years, there has been an increasing interest in the use of electrochemical methods for the treatment of recalcitrant toxic wastes [7–11]. The organic and toxic pollutants that constitute such wastes, like phenols which are present in the structure of many pesticides, are usually destroyed by anodic oxidation as a result of the production of oxidants such as hydroxyl radicals, ozone, etc. [9–12]. Electrochemical methods have been successfully utilized in the purification of olive oil wastewaters [11,12], domestic sewage [13], landfill leachate [14,15], tannery wastes [16], textile wastes [17]. 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 , OH^\bullet , O^\bullet , ClOH^\bullet , H_2O_2 , O_2 , H_2 , CO_2). The electrochemical oxidation of aqueous solutions, which contain organic matter, by the use of Ti/Pt anode, proceeds in two steps [7]. The first step is the anodic discharge of the water, forming hydroxyl radicals which are adsorbed on the active sites of the electrode surface (M[]).



After adsorption the adsorbed hydroxyl radical oxidize the organic matter.



where RO represents the oxidized organic matter which can be produced continuously by the hydroxyl radicals which are also continuously formed, since the anodic discharge of the water goes on. The radicals, OH^\bullet , O^\bullet and ClOH^\bullet have a very short life-time due to their high oxidation potential and are either form to other oxidants (such as Cl_2 , O_2 , ClO_2 , O_3 , and H_2O_2) or oxidize organic compounds (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 reasonably a long life-time and diffuse into the area away from the electrode, thus continuing the oxidation process (indirect oxidation). Effective pollutant degradation is

based on the direct electrochemical process (that takes place in an area around the electrode) because the secondary oxidants are not able to totally convert all the organic species into water and carbon dioxide. In our previous investigation [18], we found that using acid solutions, oxygen, free chlorine and possible some ozone and chlorine oxides are the main secondary oxidants, byproducts of the direct oxidation process.

Methyl-parathion (MeP; IUPAC: *O,O*-dimethyl-*O*-4-nitrophenyl phosphorothioate) is a widely used organophosphoric pesticide for crop production and fruit tree treatment. It is a very toxic substance (for all organisms) and graded to the first toxicity category according to the US Environmental Protection Agency: high risk for the health (EPAI). The acute oral LD₅₀: for rats is approximately 6 mg/kg and for male mice 24 mg/kg. The accepted daily human intake is 0.02 mg/kg body weight [19]. The accepted concentration in ground water for the European Union is 0.1 µg/l.

This paper discusses the treatment of MeP by an electrochemical method, in laboratory scale plant using an Ti/Pt electrode as anode.

2. Materials and methods

2.1. Experimental equipment

The experimental equipment is shown in Fig. 1. The electrolytic cell was a vessel (V) which contained 6 l of brine solution (H₂O + NaCl). The electrode was a cylinder made of titanium alloy. Its dimension was 14 cm in length and 1.5 cm in diameter; it was covered by platinum alloy foil approximately 0.22 mm thick. The electrode, which was placed in a perforated stainless steel 304 cylinder (14 cm in length and 8 cm in diameter) served as cathode. This construction ensured homogenous dynamic lines between anode and cathode and provided good contact of waste with the electrode. The electrode was operated at 36 A DC. The voltage was depended on the percentage of NaCl used. For 1, 2 and 3% (w/v) NaCl used, the voltages were 23, 17–18 and 14 V, respectively.

To mix the brine solution and to insure the continuous presence of unreacted organic matter close to the anode, a mixer was used in the cell. It operated at 300 rpm. The system was cooled.

2.2. Methodology

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

First treatment process: Nineteen milliliter of Folidol M, were added to the electrolytic cell with a pipette. Then 38.500 mg COD MeP were placed in the electrolytic cell also sodium chloride 1 and 2% (w/v) was used as electrolyte. In the case of 2% NaCl the pH of the brine solution was kept constant at the value of 10 (by using NaOH 0.1N). The total time for electrolysis was 30 min.

Second treatment process: Two different solutions of MeP pesticide, 3.6 and 8% (v/v) were used. Sodium chloride 1, 2 and 3% (w/v) was added as electrolyte for the 8% MeP solution and only 2% NaCl was used with the 3.6% MeP solution. The mixture was pumped

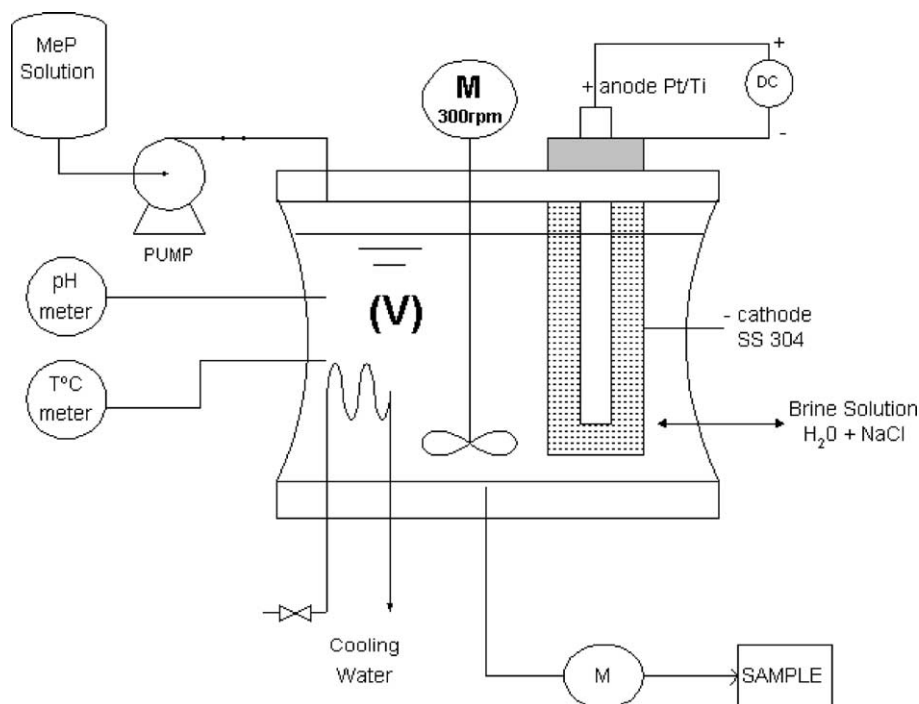


Fig. 1. Schematic of electrolytic cell used in MeP oxidation experiment.

into the electrolytic cell at a flow rate of 3 ml/min. With this flow rate, 600 mg COD/min were added to cell for the 3.6% MeP solution, and 1300 mg COD/min for the 8% MeP solution. The total time for electrolysis was 2 h. Every 15 min, an equal quantity to the inflow quantity was taken from the cell for analysis. In all cases sodium chloride was added to the electrolytic cell, at the respectively concentration.

Two experiments were run under the same conditions. In order to examine how the waste was detoxified the chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD₅) were measured, according to techniques published in Standard Methods for Examination of Water and Wastewater [20].

3. Result and discussion

As can be seen in Table 1, the utilization of electrolysis to detoxify methyl-parathion pesticide has the ability to significantly reduce the COD. This finding is in agreement with previous studies, which used the electrochemical oxidation for the treatment of different wastes, i.e. for olive oil wastewater 93% removal of COD was achieved [11], for leachate, 84% [14], for tannery wastes, 52% [16] and for textile dye wastewaters 90% [17]. In this study, almost 85% of the COD was destroyed. Furthermore, higher percentage COD

Table 1
Percentage of COD reduction during electrolysis of MeP

Treatments	Sodium chloride (%)	Input COD (mg)	Output COD (mg)	COD reduction (%)
40% MeP (30 min)	1	38,500 ± 45	6,360 ± 20	83.5
40% MeP (30 min)	2	38,500 ± 32	6,636 ± 19	82.8
3.6% MeP (120 min)	2	72,954 ± 80	6,114 ± 32	91.6
8% MeP (120 min)	1	140,736 ± 142	11,020 ± 25	92.2
8% MeP (120 min)	2	135,726 ± 130	9,726 ± 41	92.8
8% MeP (120 min)	3	137,850 ± 125	11,376 ± 22	91.7

reduction was achieved when a continuous flow rate was used (second treatment process) rather than a single input of the sample (first treatment process) was used.

Fig. 2 shows the change of pH in the brine solution during electrolysis. In all cases the initial pH of brine solution was neutral (pH ≈ 7.0). When the input COD rate was 1300 mg COD/min (8% MeP), the pH quickly became acid (pH 2.5–3.3). In contrast, when the input COD rate was 600 mg COD/min (3.6% MeP), the pH remained relatively stable in the moderate alkaline region (pH 8–6.5). The electrolysis was more effective (lower ratio kWh/kg COD_r) when the pH was in the acid range (Table 2). The continuous correction of pH to 10.0 had no positive effect at the efficiency of electrolysis (higher ratio kWh/COD_r and lower anode efficiency).

During electrochemical oxidation part of the applied electric energy is converted to heat. From previous experiments without cooling system, we found that a temperature increase to boiling levels was one result. For this reason, an adjustment of temperature to normal levels, was attempted. Fig. 3 shows the change of temperature of the brine solution during electrolysis. In the beginning, the temperature of the system increased but stabilized after 40–50 min. When 1% NaCl was used, the temperature increase was higher (40 °C) compared to 3% NaCl (25 °C). It seems that with a higher concentration of NaCl, the major part of

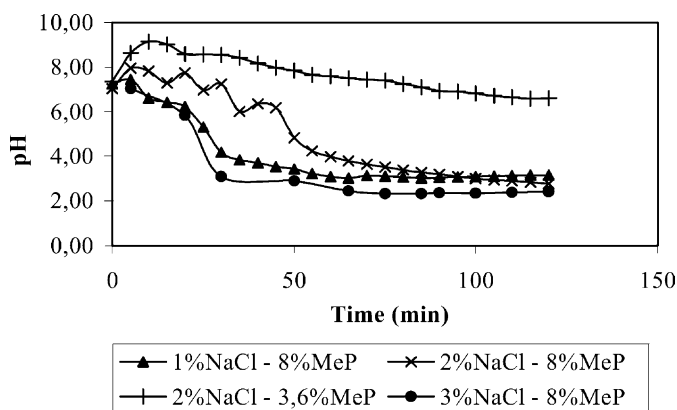


Fig. 2. Change of pH during electrolysis of MeP.

Table 2
Electrolysis parameters employed during MeP wet oxidation experiments

Treatments	COD reduction (kg)	Energy consumption (kWh)	kWh/kg COD _r	Mean anode efficiency (g h ⁻¹ sqm ⁻¹ A ⁻¹)	pH
40% MeP in 30 min (1% NaCl)	0.032	0.46	14.37	248.18	6.98
40% MeP in 30 min (2% NaCl)	0.032	0.41	12.99	227.86	10.00
3.6% MeP in 120 min (2% NaCl)	0.067	1.236	18.49	132.31	6.61
8% MeP in 120 min (1% NaCl)	0.130	1.642	12.66	253.04	3.16
8% MeP in 120 min (2% NaCl)	0.126	1.444	11.45	221.93	2.78
8% MeP in 120 min (3% NaCl)	0.126	1.027	8.12	250.26	2.42

energy generate, was used by the system, in order to destroy the organic matter rather than to increase the temperature.

The efficiency of the electrolysis system depends on the energy consumption for the reduction of 1 kg of organic matter (in terms of COD), which is one of the most important factors in the economics. Table 2 shows that the continuous flow rate of MeP, resulted in a decrease of the kWh/COD reduction ratio of approximately 10% compared to the addition of pesticides at once. Also, doubling the quantity of MeP, entering the cell under 2% NaCl, resulted in a decrease of the kWh/kg COD_r ratio of approximately 38% (Table 2 and Fig. 4). Furthermore, the increase of the percentage of NaCl from 1 to 3% improved the corresponding ratio by about 40% (case of 8% MeP). The lower ratio was found for the mixture of 8% MeP and 3% NaCl (kWh/kg COD_r ratio = 8.12). In the final sample of

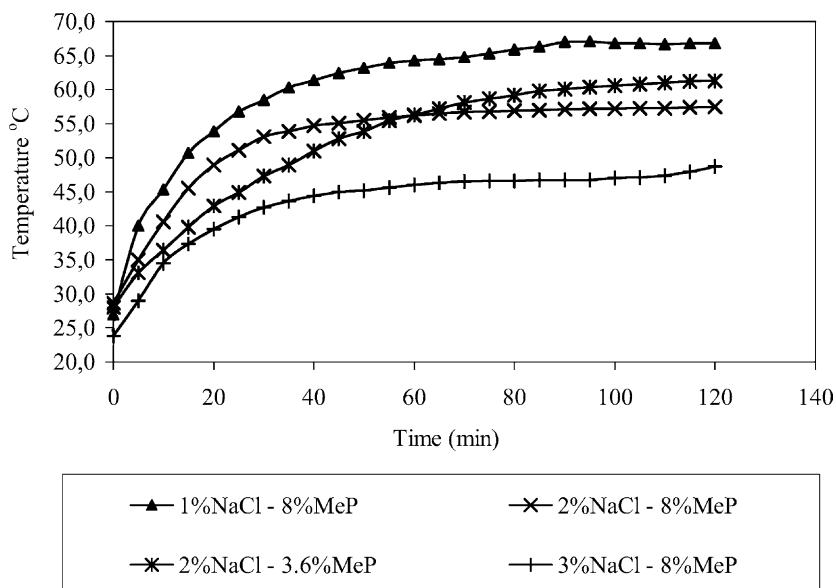


Fig. 3. Change of temperature T (°C) during electrolysis of MeP.

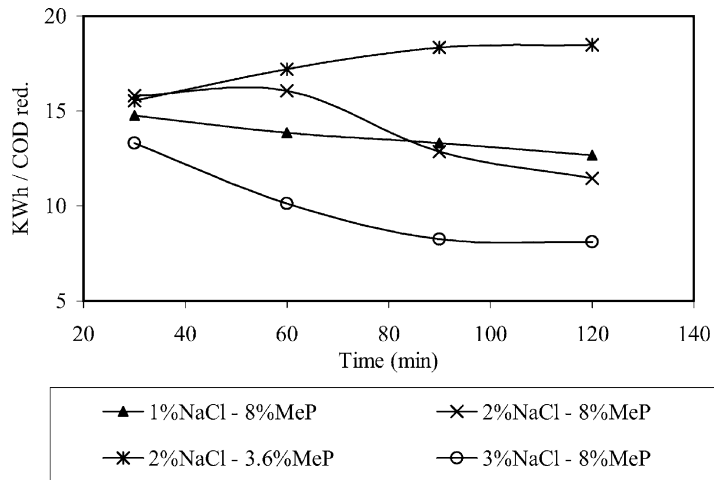


Fig. 4. Evolution of ratio kWh/COD reduction during electrolysis of MeP.

this mixture (after 2 h electrolysis) the BOD₅ was measured and was found to have been reduced about 80%. The input BOD₅ was 26830 mg while the final BOD₅ was 5443 mg.

The COD/BOD₅ ratio can be used to estimate the relative degradability of a waste. A low COD/BOD₅ ratio would indicate a large biodegradable fraction. Conversely, a waste with a high COD/BOD₅ ratio has a large nonbiodegradable fraction [21]. The use of the COD/BOD₅ ratio as an indicator of biodegradability is advantageous over the single BOD₅ measurement since this ratio also take into account the extent of the total oxidation that

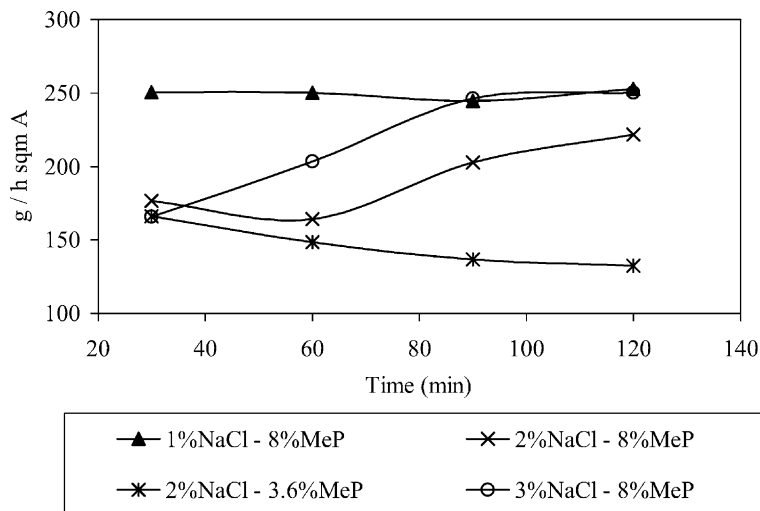


Fig. 5. Evolution of anode efficiency during electrolysis of MeP.

had occurred during electrolysis [22]. A waste with COD/BOD₅ ratio <2 can be treated by a biological system while a COD/BOD₅ ratio >5 indicates a difficult to biodegrade waste [21]. The initial ratio COD/ BOD₅ of the mixture 8% MeP was equal to 5.14 while at the end point was 2.09. This indicates that the final product had been detoxified and a biological method can be utilized.

Fig. 5 and Table 2 show the anode efficiency during electrolysis. The efficiency is reported in grams of COD removed per electrolysis time in hours, per applied ampere and per square meter of the anode. The efficiency was increased by approximately 70% when the concentration of MeP was doubled (from 3.6 to 8%) while the NaCl concentration had little or no effect on this variable. There are no significant difference between the continuous addition of high quantity of organic matter (8% MeP solution) and the initial addition (first treatment process).

4. Conclusion

This work is a first attempt to investigate the efficiency of an electrochemical oxidation system for the treatment of organophosphoric pesticides. Electrochemical oxidation is a method that has not been utilized to date for the treatment of this type of wastes. In this study, a high reduction of COD and BOD₅ of the oxidized methyl-parathion (MeP) was found. Furthermore with electrolysis an improvement of the biodegradability index (COD/BOD₅ ratio) of the investigated pesticide was achieved.

The ratio kWh/COD_T is one of the most important factors governing the economics of electrolysis. In this study, this ratio was found to be low. However, for the commercialization of this method, a further decrease of this ratio is required.

The flow rate of MeP seems to play a significant role in its degradation during electrolysis. The continuous and slow flow rate resulted in a more efficient electrolysis due to the formation of H⁺ (acid solution) and hence the enhanced destruction of organic matter. Additionally, the increase of the electrolysis time lead to a more acidic brine solution and improved the destruction effectiveness. The degradation of MeP was more effective when the pH of the brine solution was in the acid range rather than when was in the alkaline range.

The percentage of NaCl, used as electrolyte, is another important parameter for the degradation of MeP. In general, the increase of NaCl concentration increases the effectiveness of the system. From these results one can conclude that the electrolysis could be a feasible method for the treatment of toxic wastewaters with a high concentration of methyl-parathion and also could be used as a pre-treatment stage for a biological post-treatment.

References

- [1] FAO Pesticide Disposal Series, No. 9, Rome, Italy, 2000.
- [2] FAO Pesticide Disposal Series, No. 6, Rome Italy, 1997.
- [3] A. Zaleska, J. Hupka, Waste Manag. Res. 17 (1999) 220.
- [4] J.J. Pignatello, Y. Sun, Water Res. 29 (8) (1995) 1837.
- [5] T. Chen, R. Doong, W. Lei, Water Res. 37 (8) (1998) 187.
- [6] A. Kotronarou, G. Mills, M. Hoffmann, Environ. Sci. Technol. 26 (1992) 1460.

- [7] C. Comninellis, *GWA* 11 (1992) 792.
- [8] C. Comninellis, *Electrochim. Acta* 39 (11/12) (1994) 1857.
- [9] C. Comninellis, C. Pulgarin, *J. Appl. Electrochem.* 21 (1991) 703.
- [10] J. Naumczyk, L. Szpyrkowicz, M.D. De Faverri, F. Zilio-Grandi, *Proc. Safety Environ. Prot. Part B* 59 (1996) 74.
- [11] C.J. Israilides, A.G. Vlyssides, V.N. Mourafeti, G. Karvouni, *Bioresour. Technol.* 61 (1997) 163.
- [12] C.J. Israilides, A.G. Vlyssides, M. Loizidou, V.N. Mourafeti, G. Karvouni, in: *Proceedings of the 2nd Specialised Conference on Pretreatment of Industrial Wastewaters, IAWQ, Athens, Greece, 1996*, p. 840.
- [13] M. Della Monica, A. Agostino, A. Ceglie, *J. Appl. Electrochem.* 10 (1980) 527.
- [14] A. Vlyssides, P. Karlis, M. Loizidou, A. Zorpas, D. Arapoglou, *Environ. Technol.* 22 (2001) 1467.
- [15] L.C. Chang, T.C. Wen, *Water Res.* 29 (1995) 671.
- [16] A.G. Vlyssides, C.J. Israilides, *Environ. Pollut.* 1–2 (1997) 147.
- [17] A.G. Vlyssides, M. Loizidou, P.K. Karlis, A.A. Zorpas, D.J. Papaioannou, *J. Haz. Mat.* B70 (1999) 41.
- [18] A.G. Vlyssides, C.J. Israilides, M. Loizidou, G. Karvouni, V. Mourafeti, in: *Proceedings of the 2nd Specialised Conference on Pretreatment of Industrial Wastewaters, IAWQ, Athens, Greece, 1996*, p. 522.
- [19] W.J. Hayes Jr., E.R. Laws Jr., *Handbook of Pesticide Toxicology*, Academic Press, New York, NY, 1991.
- [20] APHA-AWWA-WPCF, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., American Public Health Association, Washington, DC, 1989.
- [21] R.C. Loehr, *Pollution Control for Agriculture*, Academic Press, New York, NY, 1977, p. 382.
- [22] D. Mantzavinos, D. Burrows, R. Willey, G.L. Biundo, S. Zhang, A. Livingston, I. Metcalfe, *Water Res.* 35 (2001) 3337.