

The COD Reduction of Wastewater Using Oxyl

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The main objective of this work was to investigate the effectiveness of oxyl in removing the chemical oxygen demand (COD) from wastewater. Oxyl is a strong oxidizing solution generated by the electrolysis of $w = 1\%$ NaCl brine solution from the well of the positive electrode in an electrolyzing apparatus. The electron spin resonance (ESR) spin trap technique showed that several free radical species, with high oxidation potential, are present in oxyl solution. Experimental oxidations of industrial wastewater polluted by surfactants were performed using oxyl (in the laboratory) and industrial scale yielding a COD reduction of up to 70%. The implementation of wastewater treatment using oxyl in an industrial plant may considerably reduce the water pollution tax that companies are paying for wastewater discharge. An economic feasibility study of the investment was performed, which indicated the good economic potential of the procedure.

Keywords:

Electrolyzed oxidizing (EO) water, oxyl, COD reduction, wastewater, feasibility study

Introduction

Electrolyzed oxidizing (EO) water is generated in an electrolyzing apparatus by the electrolysis of a sodium chloride solution, using a positive electrode in an anode well and a negative electrode in a cathode well. Both wells are separated by a ceramic membrane. The solution obtained from the well of the positive electrode is called oxyl. It is a strong electrolysed acid solution. Redol is obtained from the well of the negative electrode. Oxyl is reported to have a strong bactericidal effect on most pathogenic bacteria.^{1–9} It has proved to be suitable for drinking water disinfection,⁷ because the water from the anode well achieves good microbiocidal properties through the development of high available chlorine levels and high oxidation–reduction potential, ORP, (+1100 mV). *Kiura*² reported that the electrolysis of NaCl solution generates H^+ , O_2 , O_3^- and free chlorine, such as $HClO$, Cl_2 and Cl^- . Another study³ demonstrated the potential of oxyl for use as an antimicrobial agent, on account of its low pH, high ORP, and low chlorine concentration, and further study could help define more effective ways for decontaminating of alfalfa seeds and sprouts. Oxyl has the potential to be used for the decontamination of raw salmon,⁴ and it might be very effective for foliar pathogens.⁵

It was reported⁹ that 80% of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand

(BOD) reductions was achieved by the electrochemical oxidation of methyl-parathion (MeP) pesticide. Sodium chloride was added to MeP solution as electrolyte and the mixture was passed through an electrolytic cell. Due to the strong oxidizing potential of the produced chemicals, the organic pollutants were wet oxidized to carbon dioxide and water.

A few authors¹⁰ have suggested wastewater treatment with oxyl because it seems to have many advantages over other conventional disinfectants, e.g. it is non toxic, it shows good efficiency, the handling of the electrolyzing apparatus (also called diaphragmalyser) is easy, and it is flexible. As oxyl represents a promising oxidizing agent, the objective of this study was to investigate the efficiency of oxyl for COD removal from wastewater generated in a chemical plant producing cleansers and disinfectants.

Materials and methods

Oxyl was prepared in the Eurostel Demonstration unit (Model No: DEMO-30, Aquastel, Estonia)¹² electrolysis apparatus. The principle of the apparatus is presented in Fig. 1. The apparatus consists of two wells, which are separated by a ceramic membrane. Its composition is protected by a patent¹³. The positive electrode is made of Titanium, coated with Ru/Pt, installed in the first well, and the cathode is made of Platinum, coated by MnO_2 and pyrographite, installed in the second well.

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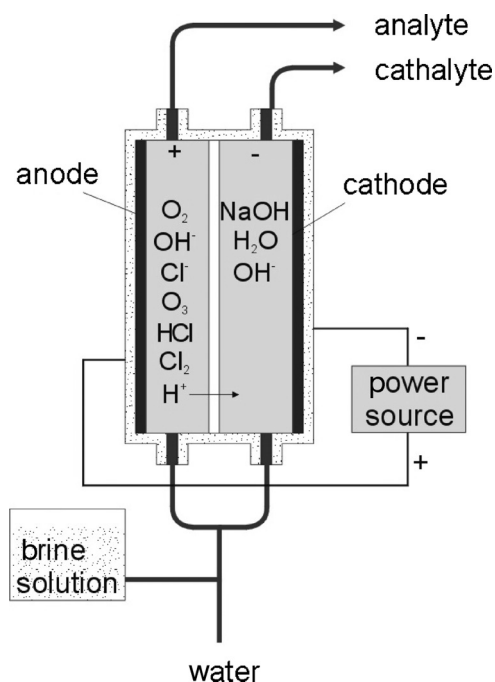
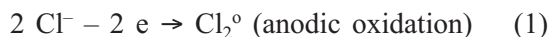
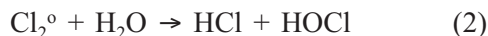


Fig. 1 – Oxyl (Analyte) solution generation

The reactions on the anode well are as follows:



And immediately:



On catode well sodium is formed:



Sodium reacts immediately with water to NaOH:



H₂-gas leaves the solution.

The brine solution was prepared as a $w = 1\%$ NaCl solution. The unit was operated at 15 A for approximately 10 min and the oxyl captured from the polypropylene discharge tube in a clean amber glass jar with a tightly fitting, screw cap lid.

Free chlorine concentrations were determined by DPD-FEAS (*N,N*-diethyl-*p*-phenylenediamine-ferrous ethylenediammonium sulphate) test kit, according to the manufacturer's specification (Merck Co., Mikro+Polo, Slovenia). pH and ORP were measured using a pH/mV meter (Iskra, Slovenia), equipped with a glass electrode and an ORP electrode. Chloride ions were determined titrimetrically by Moor titration. Conductivity was determined by a WTW conductivity meter (WTW, Mikro+polo, Slovenia). COD was determined according to ISO 6060. For ESR experiments the Bruker spectrometers ER 200 D-SRC 9/2.7, with

the data system ESP1600 and the Bruker ESP300E were used, operating at 9.6 GHz with 100 kHz modulation frequency.

Magnetic stirrer Heidolph, MR 3001 K was used for stirring of the solutions.

Experimental

Stability of oxyl

Firstly, the stability of oxyl was studied. The analyses of pH, ORP, free chlorine, conductivity, and chloride mass concentration were carried out immediately after the generation of oxyl (Table 1).

Table 1 – Main quantities determined in oxyl

Quantity	Measured value
pH	3.7
ORP V / mV	1 100
free chlorine $\gamma / \text{mg L}^{-1}$	446
conductivity $\kappa / \text{mS cm}^{-1}$	13.3
chloride $\gamma / \text{mg L}^{-1}$	6 000

After a month the oxyl was stable, only the mass concentration of free chlorine began to decrease and, consequently, the ORP value decreased slowly. Every time the oxyl was prepared, a stability test was performed by measuring the quantities shown in Table 1. The results are in agreement with the literature data.^{14,15}

Free radical species generated in oxyl after electrochemical activation were characterised by the ESR spin trapping technique. 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline *N*-oxide (DEPMPO) was used as a spin trap for the OH radicals. Adduct was formed as follows (Figure 2):

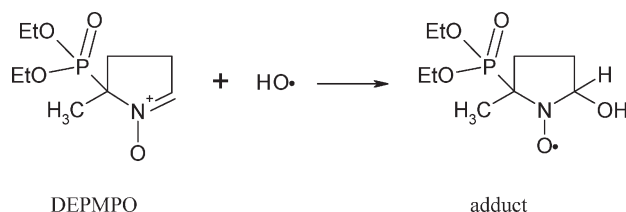


Fig. 2 – Adduct formation

Figure 3 shows the typical hydroxide adduct of the spin traps DEPMPO. The OH radicals are highly reactive and they form a stable product. The mass concentration of OH radicals is stationary, be-

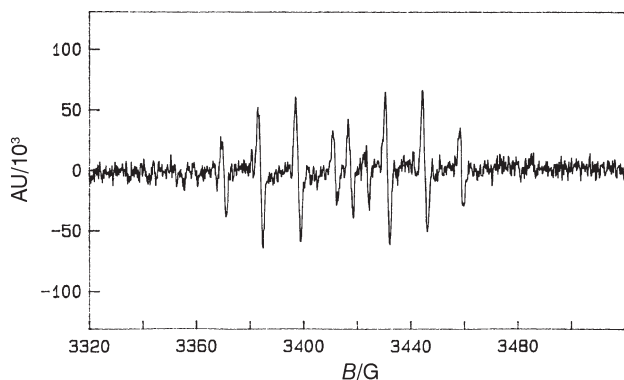


Fig. 3 – Formation of the hydroxide adducts of the spin traps DEPMPPO ESR settings: sweep width, 200 G; modulation amplitude, 1.02 G; microwave power, 20 mW; time constant, 40.96 s; receiver gain, $5 \cdot 10^5$.

cause of the equilibrium condition in which radicals are formed at the same rate, that adducts are destroyed. Hydroxyl radicals, formed in oxyl after activation in an electrolysis apparatus, have a higher oxidation potential (2.8 V) than HOCl solution (1.49 V). Hydroxyl (OH) radical is, thus, considered to be a strong oxidiser.

Treatment of organic solvents by oxyl

Three toxic organic solvents, chloroform, acetone and benzene, were selected to establish the possibility of oxidation with oxyl in order to reduce the COD value. Firstly, different amounts of oxyl (1, 10 and 20 mL) were added to 10 mL of benzene solution ($\varphi = 0.2\%$). COD and pH were measured. The reduction of COD after 20 min of stirring is presented in Figure 4. The oxidation with oxyl was also performed on acetone and chloroform, with the same amounts as by benzene solution.

The best results were achieved when treating chloroform. pH value did not change significantly, COD reduction was about 55 % after 20 mL of oxyl

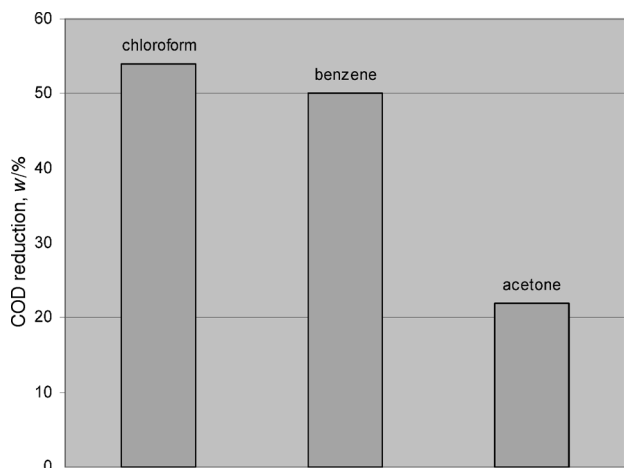


Fig. 4 – COD reduction of chloroform, benzene and acetone

was added, while, after 1 and 10 mL of oxyl was added, no improvements were noticed. COD reduction when treating benzene was about 50 % while there was just a little success with acetone – only 22 % of COD reduction.

The above results indicated that the organic pollutants can be oxidized to non-toxic compounds (like CO_2 and water) and that oxyl could be used for the treatment of some industrial wastewaters in order to efficiently reduce the COD-value.

Laboratory treatment of wastewater by oxyl

Further attention was dedicated to the wastewater treatment by oxyl. Samples were taken from the production plant of cleansers and disinfectants, where wastewater was collected in a 5 m^3 reservoir. The main objective of the investigation was to determine the quantity of oxyl and the optimum time of stirring in order to reduce the COD of the wastewater as much as possible. First of all 1 mL of oxyl was added to 1 liter of wastewater sample. COD was unchanged with regard to the untreated wastewater sample. Then 2 mL of oxyl was added to 1 liter of the same wastewater sample. The result remained the same. After 5 mL of oxyl addition, a slight COD reduction was detected (10 %). It was obvious that insufficient quantities of oxyl were added to the wastewater. A volume ratio was increased to $\psi_{\text{oxyl/water}} = 1 : 50$ and further to $\psi_{\text{oxyl/water}} = 1 : 10$. The results obtained for 500 mL of wastewater sample are presented in Table 2.

Table 2 – COD dependence on oxyl added to 500 mL of wastewater

Quantity\samples	1	2	3	4
Volume of oxyl added V/mL	0	10	25	50
pH	7.5	7.5	7.5	7.5
COD $\gamma_{\text{O}_2}/\text{mg L}^{-1}$	9 000	5 480	3 600	2 450
COD removal w/%	–	39	60	73

The COD removal was above 70 % after 50 mL of oxyl was added and about 60 % after 25 mL of oxyl was added. Only 39 % of COD was removed when 10 mL of oxyl was added. Following these results the volume ratio of oxyl to water should be at least 1:10 to reduce the COD sufficiently (more than 70%), because technological solutions, yielding significant improvements, are desired in industrial practice. Other parameters of wastewater e.g. pH, ORP, etc. changed only slightly.

A wastewater sample was taken from the reservoir after the cleansers were produced. 50 mL of oxyl was added to 500 mL of the sample and stirred for 10, 15, and 20 min at $n = 20 \text{ min}^{-1}$. COD, and the pH were measured. The results are presented in Table 3.

Table 3 – *Stirring time influence on COD*

Quantity\samples	1	2	3	4
Time of stirring t/min	0	10	15	20
pH	6.8	6.9	6.9	6.9
COD $\gamma_{\text{O}_2}/\text{mg L}^{-1}$	3 680	2 170	1 290	1 050
COD removal $w/\%$	–	59	65	71

From Table 3 it is obvious that time has a huge influence on COD reduction. After only 10 min of stirring, the COD removal was 59 %, while after 20 min of stirring, the COD value dropped to 71 %, which is a very good result. If the COD value is lowered by 70 % it means 70 % less environmental pollution and 70 % savings in the payment of environmental pollution tax.

Industrial-scale treatment of wastewater by oxyl

A wastewater sample was taken from a reservoir of 5 m³. Into the same reservoir 100 L of oxyl was added and then stirred for 20 min. After the sample was taken, another 150 L of oxyl were added once again and stirred again for 20 min, and the third sample was taken. After that, another 250 L of oxyl were added and stirred again for 20 min, and the fourth sample was taken. All four samples were analyzed. The results are presented in Table 4.

Table 4 – *COD measurements in wastewater before and after oxyl treatment*

quantity\samples	1	2	3	4
Total volume of oxyl V_{tot}/L	0	100	250	500
COD $\gamma_{\text{O}_2}/\text{mg L}^{-1}$	9 900	6 800	6 400	2 880
COD removal $w/\%$	–	31	35	71

The results obtained were the same as for sample No3, if 250 L of oxyl were added at once. The same experiment was repeated with a stirring time of 30 minutes. COD removal after the oxyl was added was nearly 70 %, which is practically the

same as after 20 min of stirring. Therefore, a stirring time of 20 min is enough to achieve a good connection between oxyl and dissolved substances in order to gain optimum conditions for high oxidation effect.

Feasibility study of wastewater treatment by oxyl in an industrial plant

The chemical plant under consideration produces cleansers and disinfectants. The plant generates 8 700 m³ of wastewater per year containing mostly surfactants, that cause high average COD value of 7 000 mg L⁻¹ O₂. This wastewater was treated by ozone in the past without considerable reduction of COD value. The treatment procedure by oxyl is proposed with a volumetric ratio of oxyl-wastewater 1:10, stirring time 20 min and $w = 1 \%$ sodium chloride solution for oxyl generation. The reduction of the COD value by 70 % is expected, i.e. from 7 000 mg L⁻¹ O₂ to 2100 mg L⁻¹ O₂, yielding a significant reduction in a company's expense for water pollution tax.

Estimation of the saving. According to the Slovenian legislation a Water Pollution Tax (*WPT*) for technological wastewater discharge is calculated as follows:

$$\text{WPT} = c_{\text{ELU}} \frac{q_v \cdot \gamma_{\text{CODav}}}{\gamma_{\text{ELU}}} \quad (1)$$

where:

- WPT – water pollution tax (EUR a⁻¹)
- q_v – volumetric flow of wastewater (ML a⁻¹)
- COD_{av} – average COD value (mg L⁻¹ O₂)
- γ_{ELU} – environmental load unit (50 kg O₂ expressed as COD)
- c_{ELU} – amount of tax per individual environmental load unit (EUR)

In the year 2004/2005 the amount of tax per individual ELU in Slovenia is 26 EUR (6 236 SIT). Calculated *WPT* for $q_v = 8.7 \text{ ML a}^{-1}$ and COD_{av} value 7 000 mg L⁻¹ O₂ amounts to 31 670 EUR a⁻¹. After the treatment with oxyl the COD_{av} value is expected to decrease to 2 100 mg L⁻¹ O₂ while the quantity of water increases for 10 % to 9.57 ML a⁻¹. The corresponding *WPT* amounts to 10 450 EUR a⁻¹ giving a saving in a environmental tax of 21 220 EUR a⁻¹. As the environmental taxes are expected to rise in the future, the saving will be even higher.

Estimation of the capital cost. The EUROSTEL EE 160 electrolysing apparatus with a capacity of 160 L h⁻¹ of oxyl was suggested by the producer.¹² Purchased cost of the equipment in the year 2004 was provided from the vendor in the amount of 9 000 EUR. 20 % was added for the equipment installation yielding a total fixed capital cost of 10

800 EUR, while the working capital was neglected. It was assumed that a 5 m³ agitated vessel is already available at the site.

Estimation of the operating cost. The required quantity of oxyl solution was estimated to 870 m³ a⁻¹ and the working time of the equipment to 6 360 h a⁻¹. The operating costs are composed of the sodium chloride and water costs for 1 % brine solution, and the electricity cost used by the equipment with the power of 0,32 kW and by 1 kW agitator (Table 5). It was assumed that no additional operators are needed to operate the facility.

Table 5 – Operating cost estimation

Raw materials and energy	Consumption	Price	Annual operating costs (EUR a ⁻¹)
NaCl	8 700 kg a ⁻¹	0.23 EUR kg ⁻¹	2 001
water	861.3 m ³ a ⁻¹	1.06 EUR m ⁻³	913
electric power	8 395 kWh a ⁻¹	0.059 EUR kWh ⁻¹	495
together			3 409

Estimation of the profitability. The payback time (t_{PB}), the net present value, (NPV) and the internal rate of return (IRR) of the project were estimated, based on the cash flow after taxes, using the 25 % tax rate. Yearly depreciation charge was estimated for a 5 year period using the straight-line method. The cash flow after taxes (F_C) resulting from the saving obtained, was calculated as follows:

$$F_C = (1 - 0.25) \cdot (21220 - 3409) \frac{\text{EUR}}{\text{a}} + 0.25 \frac{10800 \text{ EUR}}{5 \text{ a}} = 13900 \text{ EUR a}^{-1} \quad (2)$$

Payback time is calculated as:

$$t_{PB} = \frac{10800 \text{ EUR}}{13900 \text{ EUR a}^{-1}} = 0.77 \text{ a} \quad (3)$$

NPV was calculated using 10 % discount rate:

$$\text{NPV} = -10800 + \sum_{n=1}^5 \frac{13900}{(1+0.1)^n} = 41890 \text{ EUR} \quad (4)$$

The corresponding internal rate of return (IRR) is 126.5 %.

Positive NPV, high IRR, and a payback time shorter than one year indicate to a high profitability

for an investment in the proposed wastewater treatment facility. It should be mentioned, that this is not a common case, while investing money in the ecological projects on pollution control.

Conclusion

The oxidizing capacity of oxyl for COD removal in the wastewater polluted by the surfactants was investigated. It was found out that free OH radical species are generated in oxyl, which significantly contribute to its high oxidizing capacity. Experimental treatment of the wastewater from the cleansers production plant with oxyl was carried out in the laboratory- and industrial-scale yielding the COD reduction up to 70 % and, consequently, the potential for the significant reduction of water pollution tax. A feasibility study of the proposed wastewater treatment procedure showed promising economic potential. As the quantity of waste, produced by the treatment with oxyl is very low compared to other procedures, e.g. flocculation, the proposed oxyl technology is well implied by the context of sustainable development.

Future work will be oriented towards the realization of the project in the industrial environment as well as to widening the applicability of oxyl technology to the industrial wastewaters contaminated with other pollutants.

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Abbreviations

- DEPMPO – 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline *N*-oxide
 DPD-FEAS – *N,N*-diethyl-*p*-phenylenediamine-ferrous ethylenediammonium sulfate
 EO – electrolyzed oxidizing
 ESR – electron spin resonance
 IRR – internal rate of return
 MeP – methyl-parathion
 ORP – oxidation-reduction potential

Symbols

- BOD – biochemical oxygen demand, mg L⁻¹ O₂
 γ_{COD} – chemical oxygen demand, mg L⁻¹ O₂
 γ_{ELU} – environmental load unit (50 kg O₂ expressed as COD)
 F_C – cash flow after taxes, EUR a⁻¹

NPV – net present value, EUR

q_v – volume flow rate, ML a^{-1}

c_{ELU} – amount of tax per individual environmental load unit, EUR

t_{PB} – payback time, a

WPT – water pollution tax, EUR a^{-1}

Ψ – volume ratio

w – mass fraction, %

n – stirring speed, min^{-1}

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