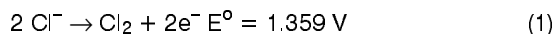


DISINFECTION OF DRINKING AND BATHING WATER WITH OXYL

An electrolysed solution of sodium chloride was examined for its disinfection potential in drinking and bathing water. The electrolysis of NaCl ($\gamma = 1\%$) in tap water was performed at room temperature using a 10 A electric current in an electrolysis apparatus. Some laboratory tests were made, initially to determine the stability and efficiency of the disinfectant. Chemical and microbiological measurements of the treated water (according to DIN 19643 for bathing water) were then carried out before and after addition of the disinfectant agent.

Electrolysed strongly acidic water containing sodium chloride was prepared in a Diaphragmalyser (Actiwa, Frenkendorf) electrolysis apparatus. The apparatus consists of two chambers, which are separated by a special ceramic diaphragm. The cathode was installed in one chamber, where alkaline solution was produced (NaOH) and the anode in the other where acidic solution was produced (HClO). The latter was assumed to be a good disinfectant and thus very interesting.

Based on the results of Brumen and Lapajne [6], the reactions are:



and



Some authors [1] confirm that hydrogen peroxide and other chlorine compounds are also produced, but there is no evidence. It is obvious from the reactions that this solution is strongly acidic. It is called oxyl.

It was determined [1] that freshly electrolysed water beside sodium ions, chlorine ions and free chlorine, also contains oxygen radicals. The findings of the Federal Office of Health [3] showed that oxyl was not toxic.

EXPERIMENTAL

All the chemicals used were pro analysis.

Author address: M. Simonič, Fakulteta za kemijo in kemijsko tehnologijo, Smetanova 17, 2000 Maribor, Slovenija
E-mail: marjana.simonic@uni-mb.si
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The pH was measured using a pH meter (MA 5740) after calibration with two buffers of pH 4 and 7 (DIN 38404-C5).

The oxidation reduction potential (ORP) was measured using a combined pH/rH meter. The conductivity was measured using a WTW conductivity meter (EN-27888).

The turbidity was measured with a Hanna turbidimeter 2100P.

The absorbance was determined using a spectrophotometer at the wavelength of 436 nm (DIN 38404 C1).

The chlorine and NO_3^- contents were determined using a Cary spectrophotometer applying standard methods (ISO 7393/2 and DIN 38405-D19).

The chemical oxygen demand (COD) was determined titrimetrically by a standard method.

The chloride (Cl^-) concentration was determined titrimetrically by standard methods. Microbiological analyses were performed by the Slovene Environmental Health Institute.

RESULTS AND DISCUSSION

We studied the stability of oxyl. We found that for more than two months the values of the ORP, pH and conductivity were practically the same. The pH value was constantly 3.1, the ORP about 1200 mV, the chloride concentration 14500 mg/L, the conductivity 35.3 mS/cm, only the chlorine concentration dropped from 220 to below 200 mg/L Cl_2 . The results are presented in Table 1.

These results showed very good agreement with measurements that were carried out at the Marburg Institute of Hygiene and Environment where small concentrations of ozone and H_2O_2 were also detected (in $\mu\text{g}/\text{litre}$). Some authors [4,7] confirmed that these compounds should not be neglected.

Numerous experiments were carried out in different German laboratories. The experiments were performed with oxyl ($\psi = 0.1$ to 0.2%) in bathing water, which means that 1 to 2 ml of oxyl were added to 1000

Table 1. Stability test of acidic solution

Parameter	Unit	Measurements	Time (days)
pH		3.1	1
ORP	mV	1200	1
chlorine	mg/L	220	1
conductivity	mS/cm	35.3	1
chloride	mg/L	14500	1
pH		3.1	2
ORP	mV	1200	2
chlorine	mg/L	220	2
conductivity	mS/cm	35.3	2
chloride	mg/L	14500	2
pH		3.1	5
ORP	mV	1200	5
chlorine	mg/L	220	5
conductivity	mS/cm	35.3	5
chloride	mg/L	14500	5
pH		3.1	10
ORP	mV	1200	10
chlorine	mg/L	215	10
conductivity	mS/cm	35.3	10
chloride	mg/L	14500	10
pH		3.1	14
ORP	mV	1200	14
chlorine	mg/L	200	14
conductivity	mS/cm	35.3	14
chloride	14500	14	
pH		3.1	30
ORP	mV	1200	30
chlorine	mg/L	190	30
conductivity	mS/cm	35.4	30
chloride	14500	30	

ml of bathing water. 250 000 pathogens in 1 ml (*Pseudomonas aeruginosa*, *Escherichia coli* and fecal coliforms) were added to the water, followed by oxyd addition and after different times (0.5 to 10 minutes) of disinfection, the number of the above mentioned three types of pathogenic microorganisms was measured. The results are presented in Figure 1.

It was found that the inactivation of *Pseudomonas aeruginosa* after 30 seconds was by 3 orders of magnitude, while *Escherichia coli* and *Enterococcus faecalis* were reduced by 4 orders a magnitude after 30 seconds. Dilution plays an important role, because the time needed for disinfection for the volume ratio ψ (oxyd/water) = 1:1000 was greater than for the volume ratio ψ (oxyd/water) = 1:250. At this volume ratio colonies of *Pseudomonas aeruginosa*, *Escherichia coli* and *Enterococcus faecalis* were no longer detected after

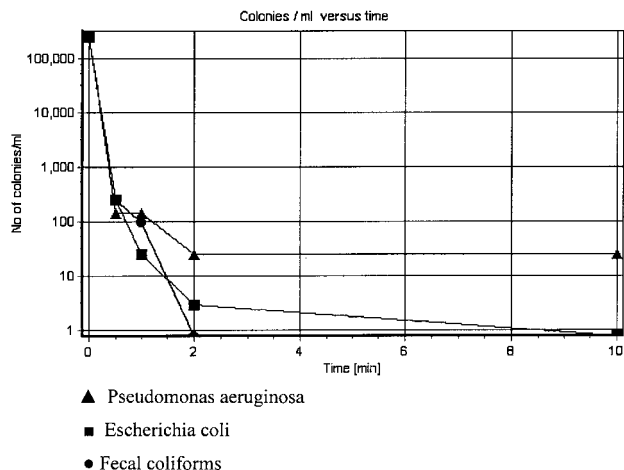


Figure 1. Sum of pathogens in bathing water after different times

30 seconds. A sufficiently high ORP value (> 700 mV), especially in tests with *Escherichia coli*, was of major importance.

These facts fulfill the requirement demanding that public health should not be put at risk by bathing water.

The current was of crucial importance for the test performance. The current value must be at least 10 A. Laboratory tests were repeated at lower currents (6.5 and 8 A) at the ratios ψ (oxyd/water) = 1:1000 and 1:500, but after 10 minutes the inactivation of *Pseudomonas aeruginosa* was only by 2 to 3 orders of magnitude.

Having made some laboratory tests, we started with practical water treatment. Drinking water was taken as filled tap water to which oxyd was added. The starting sample had the volume ratio ψ (oxyd/water) = 1:1000. The results for this sample are presented in Table 2.

The test was repeated several times and the results did not differ. Even at the volume ratios ψ (oxyd/water) = 1:500 and 1:250, the results were very similar to those presented in Table 2. The only difference was a slight increase of conductivity, from 500 μ S/cm in

Table 2. Chemical measurements of bathing water according to DIN 19643

Parameter (unit)	Allowed	Measured (No 1 before oxyd)	Measured (No 1 after oxyd)
temperature (K)	309–311	311	311
colour at 436 nm (1/m)	max 0.5	0.14	0.14
turbidity (NTU)	max 0.5	0.4	0.4
pH	max 7.6	7.3	7.3
ORP (mV)	700	700	700
NO ₃ ⁻ (mg/L)	20	19	19
COD (mg/L kMnO ₄)	max 8.0	2.0	2.0
conductivity (μ S/cm)	–	510	510
free chlorine (mg/L)	min 0.3	< 0.1	< 0.1
bond chlorine (mg/L)	max 0.2	< 0.1	< 0.1

filled water to 510 $\mu\text{S}/\text{cm}$ in treated water. All the other measured parameters did not change.

Finally, we carried out experiments in a pool with some people bathing in it. After a while oxyI was added, ψ (oxyI/water) = 1:1000 and 5 minutes later samples were taken and analysed. The results are presented in Table 3.

Table 3. Chemical measurements of bathing water according to DIN 19643

Parameter (unit)	Allowed	Measured (No 2 before oxyI)	Measured (No 2 after oxyI)
temperature (K)	309–311	311	311
colour at 436 nm (1/m)	max 0.5	0.14	0.14
turbidity (NTU)	max 0.5	0.9	0.8
pH	max 7.6	8.3	8.2
ORP (mV)	720	630	630
NO_3^- (mg/L)	20	19	19
COD (mg/L KMnO_4)	max 8.0	16.0	15.5
conductivity ($\mu\text{S}/\text{cm}$)	–	510	514
free chlorine (mg/L)	min 0.3	< 0.1	< 0.1
bond chlorine (mg/L)	max 0.2	< 0.1	< 0.1

As can be seen from Table 3, the turbidity, pH value and COD were too high, but the ORP value was too low. Neither free nor bonded chlorine were detected in the treated water.

At the same time microbiological analyses were made in accordance with DIN 19643 for bathing water. The results are presented in Table 4.

Table 4. Microbiological analyses after oxyI treatment

Parameters	Filling water	After treatment
MPN of total coliform bacteria/100 ml	0	0
Fecal coliform bacteria/100 ml	0	0
Mesophile bacteria/ml	105000	3500
<i>Pseudomonas aeruginosa</i>	0,0	

The MPN of total coliform and *Pseudomonas aeruginosa* were not detected neither in filled nor in treated water, the count of Mesophile decreased from 105000 CFU/ml to 3500 CFU/ml, which did not satisfy DIN 19643, where the count should be below 100 CFU/ml.

We decided to increase the volume ratio of oxyI to ψ (oxyI/water) = 1:500. The results remained unchanged. Then the volume ratio was lowered to ψ (oxyI/water) = 1:250, but it was still not low enough. The COD was greater than 10 mg/L KMnO_4 and also the ORP was about 500 mV.

Then the concentration of oxyI in water at which the ORP increases above 700 mV was measured. It was established that the required volume ratio was ψ (oxyI/water) = 1:9. Afterwards chemical measurements were carried out in filled and in treated water. The results are presented in Table 5.

Table 5. Chemical measurements of bathing water after DIN 19643

Parameter (unit)	Allowed	Measured (No 3 before oxyI)	Measured (No 3 after oxyI)
temperature (K)	309–311	311	311
colour at 436 nm (1/m)	max 0.5	0.14	0.10
turbidity (NTU)	max 0.5	0.9	0.4
pH	max 7.6	7.3	6.1
ORP (mV)	720	600	720
NO_3^- (mg/L)	20	19	19
COD (mg/L KMnO_4)	max 8.0	16.0	6.0
conductivity ($\mu\text{S}/\text{cm}$)	–	494	4440
free chlorine (mg/L)	min 0.3	< 0.1	< 0.1
bond chlorine (mg/L)	max 0.2	< 0.1	< 0.1

The ORP was good, but the conductivity increased tremendously and also the pH value decreased below 6.5 due to the addition of a large amount of acidic oxyI. It contained a large amount of non-electrolysed NaCl (about γ = 14 g/L of chlorine ions and about γ = 9.2 g/L of sodium ions, causing increased conductivity).

As a matter of fact we could almost speak of "sea water" and not drinking water. But, on the other hand, the COD decreased below γ = 8 mg/l of KMnO_4 .

Microbiological tests were also performed. The results are presented in Table 6.

Table 6. Microbiological test (ψ (oxyI/water) = 1 : 250)

Parameters	Filling water	After treatment
MPN of total coliform bacteria/100 ml	0	0
Fecal coliform bacteria/100 ml	0	0
Mesophile bacteria/ml	1000	300
<i>Pseudomonas aeruginosa</i>	0	0

As may be seen from Table 6, the count of Mesophile decreased from 1000 CFU/ml to 300 CFU/ml, but it should be below 100 CFU/ml. Other pathogens were not detected in the bathing water.

The experiments were repeated several times, but the chemical analyses were incredibly similar to those presented in Table 5, and microorganisms were still detected in the water in a number which was not above the infection risk in bathing water.

CONCLUSIONS

Oxyl is suitable for drinking water disinfection, but it is not suitable for bathing water disinfection. As may be seen from Table 2, all the drinking water parameters remained unchanged; for example the conductivity only increased from 0.510 to 0.514 mS/cm. The amount of chloride in the water was unchanged, if oxyl were added into water in volume ratios from ψ (oxyl/water) = 1:1000 to ψ (oxyl/water) = 1:500.

Figure 1 shows that *Pseudomonas aeruginosa*, *Escherichia coli* and fecal bacteria were inactivated at a relatively low volume ratio of oxyl in water (ψ (oxyl/water) = 1:500).

There is one more advantage: in comparison to chlorine oxyl is not toxic.

In bathing water oxyl must be added in at least the volume ratio ψ (oxyl/water) = 1:9 to attain the required ORP value for bathing water, but at the same time the concentration of chloride increased over all the limits for

drinking water and the bacteria were not inactivated sufficiently.

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IZVOD

DEZINFEKCIJA VODE ZA PIĆE I VODE ZA KUPANJE OXYLOM

(Scientific paper)

Marjana Simonič, Fakulteta za kemijo in kemijsko tehnologijo, Smetanova 17, Maribor, Slovenia,

Istraživan je dezinfekcioni potencijal elektroliziranog rastvora natrijum–hlorida u vodi za piće i vodi za kupanje. Elektrolizom smo proizveli takozvani oxyl koji ima svojstva dezinfekcionog sredstva. Upotrebili smo aparaturu za elektrolizu, a dejstvom električne struje od 10 A na rastvor NaCl ($\psi = 1\%$). U laboratoriji smo pratili stabilitet i efikasnost oxyla kao dezinfekcionog sredstva. Poslije smo izveli aplikaciju na vodi za piće tako da smo analizirali vodu hemijski i mikrobiološki prije i poslije dodatka oxyla. Na isti način izveli smo aplikaciju na vodi za kupanje nakon DIN 19643.

Key words: disinfection • Bathing water • Drinking water • Disinfection potential • Electrolysis • Ključne reči: Dezinfekcija • Voda za kupanje • Voda za piće • Potencijal dezinfekcije • Elektroliza •