Municipal Effluents Treatment Using Chlorine Dioxide and Chlorine

CORNELIU BOGATU[1]*, VASILE PODE[2], ILIE VLAICU[3], ELIZA LEONTE[1], DALILA MARSAVINA[3]

[1]National Research and Development Institute for Industrial Ecology -ECOIND Branch in Timisoara, 2, et. 2 P-ţa Victoriei, 300006, Timisoara, Romania

[2]"Politehnica" University of Timisoara, 2 P-ta Victoriei, 1900 300006, Timisoara, Romania

[3]Water Treatment Company „AQUATIM", 11A Gh.Lazar Str., 300081, Timisoara, Romania

The using of combined process consisting of chlorine dioxide and chlorine, for the treatment of municipal effluents in order to search their advanced oxidation and disinfection possibilities, was investigated in this paper. The following sets of oxidant concentrations were used, 15.0 mg/L ClO_2 + 5.5 mg/L Cl_2 (1); 10.0 mg/L ClO_2 + 3.6 mg/L Cl_2 (2); 7.5 mg/L ClO_2 + 3.0 mg/L Cl_2 (3), for the treatment of some effluent samples from wastewater treatment plant of Timişoara. Organic content of samples expressed as chemical oxygen demand, decreased due to oxidation process with 17.8 - 20.7 % during 24 h, when first set of concetrations was used (1). The efficiencies of disinfection for the removal of total coliforms, fecal coliforms and fecal streptococci ranged between 90.0 – 99.9 %, at 2 h after reagents introduction in effluent samples, and were realized with 7.0 mg/L chlorine dioxide and 3.0 mg/L chlorine. By using of combined reagents, both advanced oxidation and disinfection of wastewaters take place, allowing their safe discharge into environment.
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Keywords: municipal effluents, chlorine dioxide, chlorine, oxidation, advanced disinfection.

Used in the beginning for natural water disinfection to obtain drinking water, then chlorine was applied for disinfection of effluents from municipal wastewater treatment plants. But, using of chlorine has some disadvantages: discharge of effluents treated with chlorine means introduction of residual chlorine and chlorinated by-products, like trihalomethanes, in natural waters. Chlorine doses used for wastewater disinfection ranged between 2.6-24 mg/L [1].

Reactions of some organic compounds from municipal effluents with chlorine are vary rapid. E.g., the reaction of glyphosate [N-(phosphonomethyl)glycine] with chlorine, takes place in 5 seconds in proportion of 99%, the reaction of sulfamethoxazole is realized in 23 s in proportion of 50%, and those of dimethylamine and diethylamine in few min [2,3,4]. In effluents of municipal wastewaters treated with chlorine, were determined chloroform, 1,1,1– trichloroethane, chlorophenols, chlorobenzenes, chlorinated pyrimidines and purines [5]. Due to these aspects, alternative possibilities to chlorine using were proposed: chlorine dioxide, chlorine dioxide and chlorine, ozone [6-9].
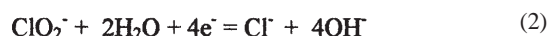
Chlorine dioxide is used both for the treatment of natural waters to obtain drinking water and of effluents from wastewater treatment plants [4,10-12]. Using of chlorine dioxide is increasing, due to its advantages:

-the disinfection capacity of chlorine dioxide is not affected by pH, in the range of 5-10;

-it does not form halogenated organic compounds, like chlorine;

-chlorine dioxide is not corrosive and is used for iron and manganese control;

-it is superior to chlorine as bactericide, virulicide and efficient for coliforms destroying [13-17].

The most important applications of chlorine dioxide to water and wastewater treatment are explained by its high reactivity with organic compounds [6,7]. Some reactions of ClO_2, like those with secondary and tertiary aliphatic amines are very rapid; reactions with humic acids and phenolic derivatives take place in few steps, during 24 h [4,18,19].

Chlorine dioxide is a selective oxidant that reacts by one electron transfer, when it is reduced to chlorite. Chlorite is the principal reaction end-product and represents about 50-70 % of used ClO_2, eq.(1), chlorate together with chloride represent about 30 %, eq. (2) and (3):

$$ClO_{2\,(aq)} + e^- = ClO_2^- \qquad (1)$$

$$ClO_2^- + 2H_2O + 4e^- = Cl^- + 4OH^- \qquad (2)$$

$$ClO_2^- + 2OH^- = ClO_3^- + H_2O + 2e^- \qquad (3)$$

Doses of used chlorine dioxide depend on wastewaters quality and they are usually between 2-7 mg/L, but sometimes they may reach 12 mg/L [21]. Now, there is an increasing use of chlorine dioxide, especially after the discovery of organohalogen compounds formation, due to chlorine reactions with organic compounds from waters [6,19,20].

The influence of the combined treatment with chlorine dioxide and chlorine, on effluent samples from wastewater treatment plant of Timişoara, for their advanced oxidation and disinfection, was searched in this paper.

Experimental part

The efficiency of combined oxidation by using of chlorine dioxide and chlorine, was tested on two effluent samples. Effluent samples represent a limit case, because wastewater treatment plant operates only with settling step. From this reason in reagents combinations, chlorine dioxide was used in concentrations higher than average values mentioned above: 15.0 mg/L chlorine dioxide + 5.5 mg/L chlorine (1), 10.0 mg/L chlorine dioxide + 3.6 mg/

L chlorine (2); 7.5 mg/L chlorine dioxide + 3.0 mg/L chlorine (3). ClO_2 was introduced first in samples and after 10 min, chlorine was added. Stock solutions of oxidants had the concentrations of 1.2 g/L chlorine dioxide and 7.5 g/L sodium hypochlorite, for chlorine.

Treatment process was investigated by analysis of oxidant concentrations evolution versus time, determination of oxidation efficiencies for organic content and decreasing of microbiological impurification from effluents, after 24 and 2 h, respectively.

Wastewater samples were characterised by physico-chemical indicators analysis, table 1. Volumes of effluent samples (1L) were treated with oxidants and the evolution of chlorine dioxide, chlorine and chlorite from samples were analysed with N,N-diethyl-p-phenylenediamine and ferrous ammonium sulphate (DPD-FAS) method, and chlorate with iodometric method [22].

By chlorine or chlorine dioxide reaction with N,N-diethyl-p-phenylenediamine in aqueous solution at pH=6.2-6.5, a red colored semiquinonic compound is formed. Method allows determination of sum for concentrations of chlorine, chlorine dioxide and chlorite, and by difference chlorite concentration may be obtained.

Reagents used for chlorine, chlorine dioxide and chlorite analysis were the followings: buffer solution with pH=6.2-6.5, consisting of 24 g Na_2HPO_4 46 g KH_2PO_4 and 800 mg EDTA, dissolved in 1 L distilled water; indicator solution: 1.1 g anhidrous sulfate of N,N-diethyl-p-phenylenediamine, 200 mg EDTA and 8 mL H_2SO_4 (1:3) in 1 L distilled water; FAS solution: 1.106 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and 1 mL H_2SO_4 (1:3) in 1 L distilled water; glycine solution, 10 g in 100 mL distilled water; sulfuric acid solution, by dissolving 5 mL concentrated H_2SO_4 in 100 mL distilled water; sodium bicarbonate solution, 27.5 g $NaHCO_3$ in 500 mL distilled water.

For chlorine dioxide analysis, in titration flask 2 mL glycine solution is introduced, 100 mL water sample, and in the other flask 5 mL buffer solution, 5 mL indicator and 200 mg EDTA: the content of the two flasks is mixed and titration with FAS until the disappearance of red colour is realized. By instantaneous reaction of glycine with chlorine chloroaminoacetic acid is formed, that allows the analysis of chlorine dioxide only.

Chlorine is determined together with chlorine dioxide, without using glycine; then, for determination of total chlorine, in the same sample 1 mL H_2SO_4 (1:3) and few KI cristals are introduced; after 2 min it is neutralized with 5 mL $NaHCO_3$ solution and is titrated with FAS until the disappearance of red color. Chlorite is determined by difference from total chlorine and cumulated concentrations of chlorine and chlorine dioxide.

For chlorate analysis, sum of chlorine dioxide, chlorine, chlorite and chlorate species was determined with iodometric method; by difference from this sum and the first three components determined above, chlorate was obtained. The following reagents were used: KBr 5%, concentrated HCl, KI, saturated solution of $Na_2HPO_4 12H_2O$, sodium thiosulfate solution, 0.10 N, starch indicator solution, 5 g/L. In titration flask are introduced 1mL KBr, 10 mL HCl and 15 mL sample; content is mixed and maintained in the dark for 20 min; 1g KI is added under mixing, and the content is transferred in titration flask that contains 25 mL of Na_2HPO_4 saturated solution; it is titrated with sodium thiosulfate in the presence of starch.

For evaluation of oxidation process, organic compunds from effluent samples were determined as global parameters, like chemical oxygen demand (COD) and absorptions measurement, at λ = 254 nm, (A_{254}).

Disinfection process was investigated by the treatment of some effluent samples with the combinations of the two oxidants for 2 h; then, samples were treated with an excess of 0.1N sodium sulphite, for quenching of residual oxidants. Microbiological analysis were undertaken for fecal coliforms, total coliforms, and fecal streptococci. These indicators were determined by membrane filtration tehnique, using a filter with 0.45 μm pore size [21, 22].

Results and discussion

Physico-chemical indicators for effluent samples from wastewater treatment plant, are presented in table 1. Organic content exceeds maximum allowable level for their discharge in natural waters, 125 mg O_2/L (HG 352.2002 - NTPA 001).

The evolution of oxidants concentrations versus contact time is presented in figures 1-6. For effluent sample l treated with the first reagents combination, 15.0 mg/L chlorine dioxide followed by 5.5 mg/L clorine, after 60 min 5.7 mg/L chlorine dioxide was consumed (38%), figure 1. Chlorine dioxide was consumed especially in the first 6 h, 9.8 mg/L (65.3%). Then, its concentration decreased slowly up to 1.4 mg/L, after 24 h.
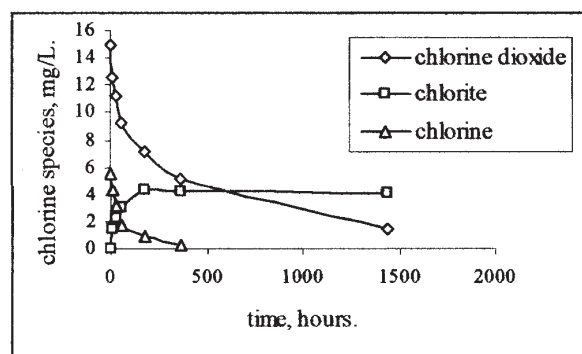

Fig. 1 Variation of ClO_2, ClO_2^- and Cl_2 concentrations versus time, for the treatment of effluent l with 15.0 mg/L ClO_2 and 5.5 mg/L Cl_2

Table 1
PHYSICO-CHEMICAL INDICATORS FOR EFFLUENT SAMPLES FROM WASTEWATER TREATMENT PLANT OF TIMISOARA

Indicator	sample l	sample ll
pH	7.25	7.15
COD, mg O_2/L	185	255
total suspended solids, mg/L	232	275.4
total nitrogen, mg/L	7.5	8.2
ammonia (NH_4^+), mg/L	4.9	5.6
nitrates, mg/L	10.5	11.2
nitrites, mg/L	0.020	0.01
chlorides, mg/L	75.0	92.0
total phosphorus, mg/L	1.5	1.8
iron, mg/L	0.10	0.20
A_{254}, cm^{-1}	0.72	0.69
total coliforms /100mL	-	160000
fecal coliforms /100mL	-	43800
fecal streptococci /100mL	-	17200

Chlorite formed due to chlorine dioxide introduced in waters, represents about 60% of intial oxidant concentration; from 13.6 mg/L chlorine dioxide consumed during 24 h, 8.1 mg/L chlorite is formed. But, chlorite concentration determined in sample after this time was 4.1 mg/L, table 2. Smaller value is explained by its partial conversion in chlorate and chloride, reactions (2) and (4). After 24 h, the analysed chlorate concentration was 3.4 mg/L; initially, chlorate was not present in effluent samples.
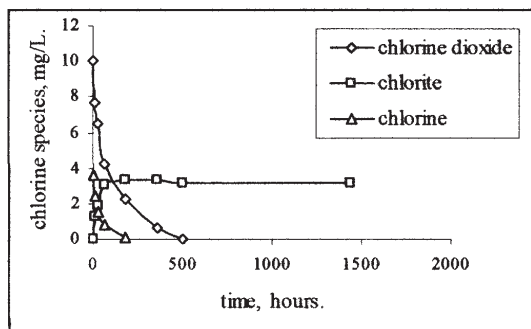
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Fig. 2. Variation of ClO_2, ClO_2^- and Cl_2 concentrations versus time, for the treatment of effluent 1 with 10.0 mg/L ClO_2 and 3.6 mg/L Cl_2
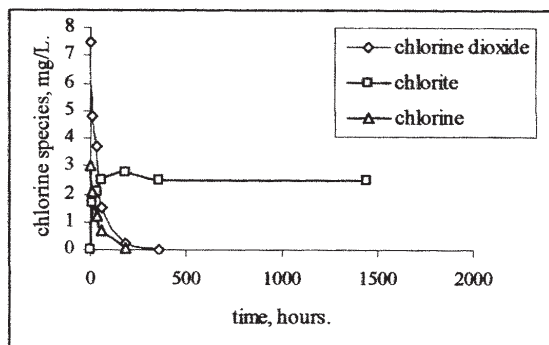

Fig. 3. Variation of ClO_2, ClO_2^- and Cl_2 concentrations versus time, for the treatment of effluent 1 with 7.5 mg/L ClO_2 and 3.0 mg/L Cl_2
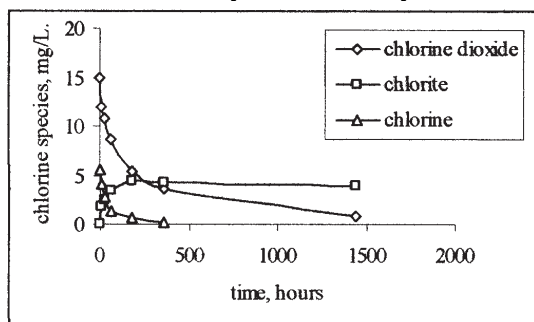

Fig. 4. Variation of ClO_2, ClO_2^- and Cl_2 concentrations versus time, for the treatment of effluent ll with 15.0 mg/L ClO_2 and 5.5 mg/L Cl_2

The evolution of chlorine added 10 min after chlorine dioxide, sustains the above findings: chlorine consumption was almost complete during 6 h; after this time, residual value of chlorine was 0.25 mg/L. Formation of chlorate took place by reaction between chlorite and free chlorine:

$$ClO_2^- + Cl_2 + H_2O = ClO_3^- + 2Cl^- + 2H^+ \qquad (4)$$
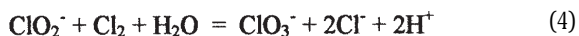
By the treatment of effluent sample 1 with the concentrations of 10.0 mg/L ClO_2 + 3.6 mg/L Cl_2 (2) and 7.5 mg/L ClO_2 + 3.0 mg/L Cl_2 (3), a similar process was revealed, figure 2 and 3. For reagent combination (2), after six hours 0.60 mg/L residual chlorine dioxide was determined, and for combination (3) reaction was complete in three hours. In both cases, chlorite determined after 24 h in samples had smaller values, than those formed from used chlorine dioxide.

In case of effluent sample ll and the three oxidant combinations, the following evolutions took place:

-chlorine dioxide was consumed almost entirely, and after 24 h were determined 0.85 mg/L, figure 4;
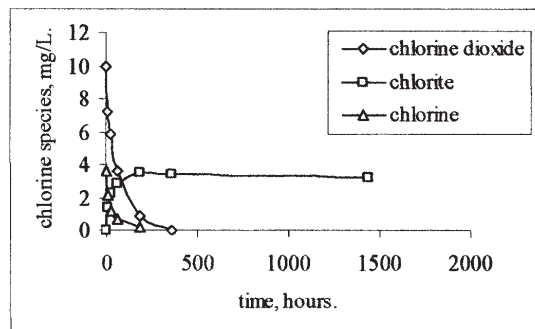

Fig. 5. Variation of ClO_2, ClO_2^- and Cl_2 concentrations versus time, for the treatment of effluent ll with 10.0 mg/L ClO_2 and 3.6 mg/L Cl_2
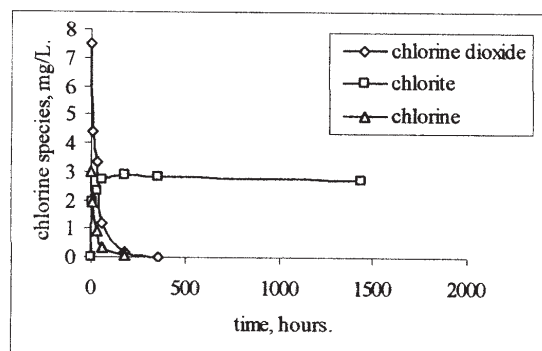

Fig. 6. Variation of ClO_2, ClO_2^- and Cl_2 concentrations versus time, for the treatment of effluent ll with 7.5 mg/L ClO_2 and 3.0 mg/L Cl_2

-for reagent combinations (2) and (3), ClO_2 was consumed in 6 and 3 h, respectively, figure 5 and 6;

-chlorine reacted completely in 6 h for combination (1) and in 3 h for (2) and (3). By combined using of oxidants, residual concentrations of chlorine are decreased, due to introduction of smaller chlorine doses.

Chlorite followed the same evolution as above: after 24 h it was determined in smaller concentrations than those resulted from chlorine dioxide, due to its partial conversion to chlorate, table 2. In these processes, the reactions of oxidants with organic matter and the influence of light, may affect the distribution of chlorine species [11].

The existence of free residual chlorine in effluents, shows the presence of some organic pollutants very reactive with this oxidant. From this reason, and due to chlorine:ammonia small mass ratio, ammonia concentrations did not decrease significantly; after 24 h and the reagents combination with 5.5 mg/L chlorine, in effluents were determined 4.4 mg/L (l) and 5.2 mg/L (ll), respectively.

To reveal oxidant effect on organic content from effluent samples, chemical oxygen demand (COD) and ultraviolet absorptions measured at $\lambda = 254$ nm, after 24 h were determined, table 3. Maximum yields were 17.8 % for sample l and 20.7% for sample ll, when reagents combination (1) was used. Measurement of ultraviolet absorptions, showed also advanced oxidation of organic compounds from treated effluents, 20.8 % and 28.9 %, respectively.

Microbiological analysis of effluent sample ll revealed for the number colonies, the values presented in table 1. These are 2-3 times higher than the maximum allowable values for surface waters of category A3, in Romania. (HG 100/2002), table 4. Samples from this effluent (1L) were treated with the three mentioned combinations of oxidants, for 2 h. The results of microbiological analysis undertaken after treatment, are presented in table 4.

Table 2

CHLORITE CONCENTRATIONS FORMED FROM CONSUMED
CHLORINE DIOXIDE (1); CHLORITE AND CHLORATE CONCENTRATIONS
DETERMINED IN SAMPLES, 24 h AFTER TREATMENT (2)

samples / oxidant combinations	time, 24 hours		
	(1) ClO_2^- (mg/L)	(2) ClO_2^- (mg/L)	(2) ClO_3^- (mg/L)
l:15.0 mg/L ClO_2 + 5.5 mg/L Cl_2	8.1	4.1	3.4
l:10.0 mg/L ClO_2 + 3.6 mg/L Cl_2	5.6	3.2	2.7
l: 7.5 mg/L ClO_2 +3.0 mg/L Cl_2	4.5	2.5	2.2
ll:15.0 mg/L ClO_2 +5.5 mg/L Cl_2	8.6	3.9	4.1
ll:10.0 mg/L ClO_2 +3.6 mg/L Cl_2	6.0	3.2	3.2
ll: 7.5 mg/L ClO_2 +3.0 mg/L Cl_2	4.5	2.7	1.9

Table 3

EFFICIENCIES OF ORGANIC CONTENT OXIDATION FROM EFFLUENT SAMPLES,
EXPRESSED AS PERCENTS OF COD (mgO$_2$/dm^3) AND A$_{254}$ (cm^{-1})
DECREASING, 24 h AFTER TREATMENT

samples / oxidant combinations	CCO-Cr, mg O_2/L	η, %	A $_{254}$ cm^{-1}	η, %
l :15.0 mg/l ClO_2 + 5.5 mg/L Cl_2	152	17.8	0.57	20.8
l :10.0 mg/L ClO_2 + 3.6 mg/L Cl_2	169	8.6	-	-
l : 7.5 mg/L ClO_2 + 3.0 mg/L Cl_2	175	5.4	-	-
ll:15.0 mg/L ClO_2 + 5.5 mg/L Cl_2	202	20.7	0.49	28.9
ll:10.0 mg/L ClO_2 + 3.6 mg/L Cl_2	214	16.0	-	-
ll: 7.5 mg/L ClO_2 + 3.0 mg/L Cl_2	238	10.5	-	-

Table 4

VALUES OF MICROBIOLOGICAL INDICATORS FOR EFFLUENT
SAMPLES II AFTER TREATMENT WITH CHLORINE DIOXIDE AND CHLORINE,
OXIDANT COMBINATIONS (1), (2) AND (3); MAXIMUM ALLOWABLE VALUES FOR
SURFACE WATERS, CATEGORIES A1, A2, A3

indicator	number of colonies					
	(1)	(2)	(3)	A1	A2	A3
total coliforms / 100 mL	90	230	9180	50	5000	50000
fecal coliforms / 100 mL	90	130	3450	20	2000	20000
fecal streptococci / 100 mL	60	170	1720	20	1000	10000

Table 5

EFFICIENCIES OF EFFLUENT SAMPLES LL DISINFECTION WITH REAGENTS;
TC – TOTAL COLIFORMS, FC – FECAL COLIFORMS, FS – FECAL STREPTOCOCCI

samples / oxidant combinations	η, % CT	η, % CF	η, % SF
15.0 mg/L ClO_2 + 5.5 mg/L Cl_2 (1)	99.9	99.8	99.6
10.0 mg/L ClO_2 + 3.6 mg/L Cl_2 (2)	99.8	99.7	99.0
7.5 mg/L ClO_2 + 3.0 mg/L Cl_2 (3)	94.2	92.1	90.0

It may be seen that an advanced disinfection process took place, with efficiencies of 90.0- 99.9 %, table 5. To realize these yields, about 7.0 mg/L chlorine dioxide and 3.0 mg/L chlorine were consumed, in 2 h. The results are similar with those determined in experiments at pilot level, by using of chlorine dioxide [21]. By combined using of chlorine dioxide and chlorine a synergic effect is estimated [6].

The values of microbiological indicators determined for the effluent samples treated with reagent mixtures (1) and (2), are much smaller than maximum allowable for A2 category of surface waters. In case of treatment with reagent mixture (3), microbiological indicators are about 5 times smaller than maximum allowable for A3 category of surface waters. These results show that by using as a final treatment step, the process improves the quality of effluents.

Conclusions

Oxidation of organic pollutants and disinfection efficiency of effluent samples from a municipal wastewater treatment plant, by using of an innovative process consisting of succesive application of chlorine dioxide and chlorine, were investigated. Effluent samples were treated by using of the following combinations of reagents: 15.0 mg/L chlorine dioxide and 5.5 mg/L chlorine (1), 10.0 mg/L chlorine dioxide and 3.6 mg/L chlorine (2); 7.5 mg/L chlorine dioxide and 3.0 mg/L chlorine (3).

Chlorine dioxide consumptions during 24 h were 13.8 mg/L and 14.1 mg/L and chlorine was consumed almost entirely after 6 h, for reagent mixture (1). For the other two combinations, (2) and (3), oxidants consumption was complete in 3-6 h after their introduction in effluent samples.

The efficiencies of organic compounds oxidation, determined by analysis of chemical oxygen demand, were 5.4-20.7% after 24 h , depending on oxidant concentrations. Advanced oxidation process was also revealed by decreasing of absorptions measured at 254 nm, with 20.8 - 28.9 %.

Microbiological analysis undertaken after the treatment of effluent samples with chlorine dioxide in combination with chlorine for two hours, showed efficiencies of 90.0-99.9% for destroying of total coliforms, fecal coliforms and fecal streptococci.

The use of the combined oxidation by application of innovative process, allowed advanced disinfection of municipal effluents and realization of requirements for their safe discharge in environment.

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