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Water purification

CHLORINE DIOXIDE SYNTHESIS AND ITS ANALYSIS BY CHEMICAL METHODS

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Abstract. Chlorine dioxide synthesis by two methods, solid-solid reaction of potassium chlorate with oxalic acid and hydrochloric acid reaction with sodium hypochlorite and sodium chlorite, and its chemical analysis are presented in this paper. In the first case, the increasing of reaction mixture temperature up to 70°C reduced the time for reaction initiation and the yield of the process was about 98.4%; in the second case, a little influence of temperature on the chlorine dioxide generation was determined, but an acidity excess from 5 to 15% over stoichiometric quantity increased the chlorine dioxide yield up to 90.5%. Relative standard deviation determined for solutions with 1.0, 2.0, 5.0 and 10.0 mg/l chlorine dioxide ranged in 2.2-8.5% by iodometric method, and 1.2-8.4% for DPD-FAS method. In chlorine dioxide solutions produced by hydrochloric acid-sodium hypochlorite-sodium chlorite method, the concentrations of inorganic species were as follows: chlorite 94.0-105.5 mg/l, chlorate 103.0-120.0 mg/l, and chlorine was absent; in those produced by solid-solid reaction, was not detected the presence of these species. By use of solid-solid reaction, chlorine dioxide may be easily applied on-site for water and liquid wastes treatment.

Keywords: solid-solid reaction, chlorine dioxide, successive analysis, iodometric and DPD-FAS methods.

AIMS AND BACKGROUND

Chlorine dioxide is an important compound discovered by Sir Humphrey Davy in 1814. It has been used at a water potable facility at Niagara Falls, N.Y., in 1944, to control taste and odour. In the last fifty years, chlorine dioxide was

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applied in water treatment as an oxidant and disinfectant in USA, Canada and Europe, both alone and in combination with chlorine, chloramines and ozone. About 700 utilities (Brussels, Toulouse, Berlin, Vienna, Zurich, etc.) use ClO_2 for pre-disinfection, post-disinfection, control of iron and manganese, of hydrogen sulphide and phenolic compounds. Daily production of chlorine dioxide is about 2200 t (Refs 1-5).

Chlorine dioxide is a small, volatile and powerful molecule. Generally, it is not used in gaseous form due to its instability; concentrated aqueous solutions of chlorine dioxide will release it in atmosphere. One of the most important properties of ClO_2 is its great solubility in water: 2.9 g/l at 20°C and 10 g/l in cold water; chlorine dioxide does not react with water: it is only dissolved in water. In water solutions, chlorine dioxide is easily decomposed in redox reactions and by-products formed are: chlorite (50-70%), chlorate and chloride (30%).

The most important application of chlorine dioxide to water and waste water treatment is due to its high reactivity versus organic compounds. It is a highly selective oxidant by one electron transfer mechanism, when it is reduced to chlorite[6–9].

Chlorine dioxide is a powerful disinfectant. It is equal or superior to chlorine as bactericide on a mass-dose basis. Its germicidal efficiency is constant over a broad pH range: at pH = 6-9 range, chlorine dioxide is at least twice as effective as free chlorine at pH = 6.

ClO_2 action against bacteria, viruses and algae is maintaning in the absence of light about 48 h: thus, the security of water distribution network is assured. Its concentration leaving water treatment plant must be less than 0.8 mg/l and chlorite in the distribution system less than 1.0 mg/l, due to harmful effects[9–12].

There are a few methods for chlorine dioxide generation. One type of methods uses reaction of sodium chlorite with: hydrochloric acid – equation (1); chlorine – equation (2); hydrochloric acid and sodium hypochlorite – equation (3), as follows:

$$5ClO_2^- + 4HCl \rightarrow 4ClO_2 + 5Cl^- + 2H_2O \quad (1)$$

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \quad (2)$$

$$NaOCl + 2HCl + 2NaClO_2 \rightarrow 2ClO_2 + 3NaCl + H_2O \quad (3)$$

The yield for reaction (3) may reach 95-99%, like in GENEROX system[6].

The other group of methods uses sodium chlorate and sulphuric acid:

$$2NaClO_3 + 2H_2SO_4 + 2NaCl \rightarrow 2ClO_2 + Cl_2 + 2Na_2SO4 + 2H_2O \quad (4)$$

$$2NaClO_3 + H_2SO_4 + H_2O_2 \rightarrow O_2 + 2ClO_2 + Na_2SO_4 + 2H_2O \quad (5)$$

Chlorine dioxide synthesis by two methods: solid-solid reaction of potassium chlorate with oxalic acid, and by hydrochloric acid reaction with sodium hypochlorite and sodium chlorite and also its chemical analysis in water solutions are presented in this paper.

EXPERIMENTAL

Preparation of chlorine dioxide by solid-solid reaction of potassium chlorate (9.8 g) with oxalic acid (24.5 g), was realised corresponding to the reaction:

$$2KClO_3 + H_2C_2O_4 \rightarrow 2ClO_2 + 2KHCO_3 \quad (6)$$

in a flask, connected to absorption vessels; gaseous chlorine dioxide was captured in distilled water. In order to appreciate the temperature influence on the reaction yield, the preparation was undertaken at three temperatures: 30, 50 and 75°C.

Analysis of obtained solution was realised by iodometric method; mean value of solution concentration was 4.2 g/l. From this, working solutions were prepared by dilution in order to comparative analysis of ClO_2 by two methods.

For synthesis of chlorine dioxide by the reaction between sodium chlorite, hydrochloric acid and sodium hypochlorite, the following solutions were used: sodium chlorite 25.0%, sodium hypochlorite 10.0%, hydrochloric acid 32.0%. The solutions introduced in a 500-ml flask had the following amounts: chlorite – 20.0, 25.0, 30.0 g; hypochlorite – 8.2, 10.3, 12.3 g; hydrochloric acid – 8.5, 9.0, 9.5 g; the quantities of chlorite and hypochlorite are those corresponding to stoichiometry, but those of hydrochloric acid are in excess above stoichiometry with 5.0, 10 and 15%. The working temperatures were 30, 40, 50 and 70°C. By this 'three-reagent method', the process takes place as follows:

$$2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + H_2O + 3NaCl \quad (7)$$

Iodometric and DPD-FAS standardised methods were used for chlorine dioxide analysis[9]. The principle for chlorine dioxide measurement purity in presence of other species is based on the reactions, which are pH dependent:

$$Cl_2 + 2\,I^- = I_2 + 2\,Cl^- \qquad pH = 7 \quad (8)$$

$$2\,ClO_2 + 2\,I^- = I_2 + 2\,ClO_2^- \qquad pH = 7 \quad (9)$$

$$2\,ClO_2^- + 8\,I^- + 8\,H^+ = 4\,I_2 + 2\,Cl^- + 4\,H_2O \qquad pH = 2 \quad (10)$$

$$2\,ClO_2 + 10\,I^- + 8\,H^+ = 5\,I_2 + 2\,Cl^- + 4\,H_2O \qquad pH = 2 \quad (11)$$

$$ClO_3^- + 6\,I^- + 6\,H^+ = 3\,I_2 + Cl^- + 3\,H_2O \qquad pH = 0.1 \quad (12)$$

From equation (9), it may be pointed out that 1 mol of iodine and 2 mol of chlorite are formed at pH = 7; from these 2 mol of chlorite, 4 mol of iodine will be produced at pH = 2, equation (10). In fact, equation (11) is the sum of equations (9) and (10) and it shows that the ratio of iodine formed at the two pH values is 1:5; so, 1/5 of chlorine dioxide will be determined at pH = 7 and 4/5 – at pH = 2.

In case of iodometric method, by sodium thiosulphate titration in the presence of starch indicator solution, in one water sample chlorine dioxide, chlorine and chlorite are determined; in the second sample – chlorine and chlorite, and in the third sample – chlorine, chlorine dioxide, chlorite and chlorate. This method can be applied for solutions of chlorine species with 0.1-100 mg/l, for their succesive analysis.

By use of N,N-diethyl-*p*-phenylenediamine (DPD) as an indicator and ferrous ammonium sulphate (FAS) as a titrant, the determination of chlorine dioxide, chlorite, free and combined chlorine, is possible. When glycine is introduced in water samples, free chlorine is rapidly converted into chloroaminoacetic acid, without any effect onto chlorine dioxide. In three different samples chlorine dioxide, chlorite, and chlorine are determined.

RESULTS AND DISCUSSION

The yields determined for chlorine dioxide synthesis by solid-solid reaction between potassium chlorate and oxalic acid are presented in Table 1. Increasing the temperature of solid mixture to 50-75°C decreased the time for reaction initiation from 6-7 h at 40°C to about 3 h at 70°C. After this time, the white solid mixture from reaction vessel became slight green-yellow and small gas quantities begin to bubble into distilled water vessels. The reaction rate may be increased by introduction of a few distilled water drops into solid mixture.

Table 1. Yields for chlorine dioxide synthesis by solid-solid reaction of potassium chlorate with oxalic acid

Sample	Temp. (°C)	$KClO_3$ (g)	$H_2C_2O_4$ (g)	ClO_2, η%	
				KI	DPD
1	40	25.0	9.4	95.0	93.4
2	50	25.0	9.4	97.2	96.5
3	75	25.0	9.4	98.4	97.0

The efficiencies for ClO_2 synthesis determined by iodometric method are between 95.0-98.4% and by DPD-FAS method 93.4-97.0%. By this method, pure solutions of chlorine dioxide were obtained, without chlorite and chlorate: checking of these two species with iodometric and DPD-FAS procedures showed their absence (Table 2). The concentrated solutions of chlorine dioxide obtained by solid-solid reaction were used for preparation of working solutions for their analysis by the two mentioned methods (Tables 3 and 4).

Table 2. Chlorite and chlorate concentrations in chlorine dioxide solutions prepared by three-reagent method (a) and solid-solid reaction (b)

Sample	ClO_2	ClO_2^- (mg/l)	ClO_3^- (mg/l)	Cl_2 (mg/l)
1	3.4 g/l (a)	94.0	103.0	0.0
2	3.9 g/l (a)	97.5	114.2	0.0
3	4.4 g/l (a)	105.5	120.0	0.0
4	4.2 g/l (b)	0.0	0.0	0.0

Table 3. Analysis of chlorine dioxide in water solutions by iodometric method

No sample	ClO_2 (mg/l)			
	1.0	2.0	5.0	10.0
1	1.05	1.95	4.85	9.75
2	1.10	2.05	5.15	9.70
3	1.15	1.90	4.90	10.30
4	1.10	1.85	4.80	10.20
5	0.90	1.90	4.95	9.85
6	1.05	1.95	4.80	9.60
7	0.90	1.95	4.90	9.70
Mean value	1.04	1.94	4.91	9.91
Standard deviation	0.09	0.06	0.11	0.24
Relative standard deviation (%)	8.60	3.10	2.20	2.40

Table 4. Analysis of chlorine dioxide in water solutions by DPD-FAS method

No sample	ClO_2 (mg/l)			
	1.0	2.0	5.0	10.0
1	0.95	1.95	5.00	9.80
2	0.95	1.95	5.10	10.10
3	1.10	1.90	4.90	10.15
4	1.05	2.10	4.95	10.05
5	0.90	2.05	5.10	9.95
6	1.10	2.10	4.90	9.85
7	0.95	2.00	5.05	9.75
Mean value	0.95	2.00	4.95	9.95
Standard deviation	0.08	0.07	0.06	0.14
Relative standard deviation (%)	8.40	3.50	1.26	1.40

Synthesis of chlorine dioxide by three-reagent method, sodium hypochlorite-hydrochloric acid-sodium chlorite, showed a little influence of temperature on the reaction yield: 90.6% at 30°C and 91.5% at 50°C. The increasing of reaction mixture temperature must not exceed 100°C, due to decomposing of chlorine dioxide to chlorine. But, acidity of reaction mass increases the reaction yield, e.g. for an excess of hydrochloric acid of 5.0% over stoichiometry the yield in chlorine dioxide is 81.8% and for 15.0% excess (pH ≅ 2), the yield is 90.5% (Table 2). The necessary time to obtain maximum concentrations of chlorine dioxide in water solutions was about 5-6 h.

Table 5. Yields for chlorine dioxide synthesis by three-reagent method: hydrochloric acid, sodium hypochlorite and sodium chlorite

Sample	Temp.(°C)	$NaClO_2$ (g)	NaOCl (g)	HCl (g)	ClO_2, η%	
					KI	DPD
1	30	20.0	8.2	8.5	81.8	80.3
2	30	25.0	10.3	10.6	88.5	87.1
3	30	30.0	12.3	12.7	90.6	92.3
4	40	20.0	8.2	9.0	82.0	81.2
5	40	25.0	10.3	11.1	86.5	83.4
6	40	30.0	12.3	13.3	91.0	90.8
7	50	20.0	8.2	9.5	84.7	85.6
8	50	25.0	10.3	11.6	87.0	86.8
9	50	30.0	12.3	14.0	91.5	90.3
10	70	20.0	8.2	9.5	85.0	83.1
11	70	25.0	10.3	11.6	87.5	89.2
12	70	30.0	12.3	14.0	88.0	90.3

The concentrations of chlorine dioxide solutions ranged in the limits of 3.4-4.4 g/l (Table 2); these values are in the range of those mentioned in the literature 2.0-5.0 g/l.

Chlorite and chlorate ions concentrations, in solutions of chlorine dioxide prepared by three-reagent method, ranged between 94.6-105 and 103.5-120.0 mg/l, respectively. In ClO_2 solutions prepared by solid-solid reaction these ions were absent.

For comparative analysis of chlorine dioxide by the two chemical methods, the following solutions were took into consideration: 1.0, 2.0, 5.0 and 10.0 mg/l. Relative standard deviation ranged in 2.2-8.6% for iodometric method and 1.2-8.4% for DPD-FAS method (Tables 3 and 4).

Synthesis of pure chlorine dioxide by solid-solid reaction of potassium chlorate with oxalic acid may be easily used both in case of small utilities for water and waste water treatment and for on-site treatment of organic liquid wastes.

CONCLUSIONS

Chlorine dioxide was prepared in laboratory, by solid-solid reaction of potassium chlorate with oxalic acid and by three-reagent method using sodium hypochlorite-hydrochloric acid-sodium chlorite, with yields of 98.4 and 90.6%, respectively. Concentration of prepared chlorine dioxide in water solutions ranged between 3.4-4.4 g/l.

Pure solutions of chlorine dioxide were obtained by solid-solid reaction; in case of three-reagent method chlorite (94.6-105 mg/l) and chlorate (103.5-120.0 mg/l) were detected.

The analysis of chlorine dioxide in solutions of 1.0-10.0 mg/l by iodometric and DPD-FAS methods showed closed values for relative standard deviation: 2.2-8.6 and 1.2-8.4%, respectively. By use of solid-solid reaction, chlorine dioxide may be easily applied on-site for water and liquid wastes treatment.

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