

Removal of benzene homologous compounds with chlorine dioxide

Chen Hui, Wei Dongbin

Chemistry Department, Northwest Normal University, Lanzhou 730070, China

Wang Shuyan, Zhu Mingyang, Liu Zhaochang

Department of Environmental Engineering, Tsinghua University, Beijing 100084, China

Keng Zhu

Chemistry Department, Peking University, Beijing 100871, China

Abstract—Chlorine dioxide composite disinfectant generator that produces a mixture of the oxidant gases comprising chlorine dioxide, chlorine, ozone and hydrogen peroxide through electrolyzing salt, is widely utilized in China presently. The experiments in the paper focused on the removal of benzene homologous compounds such as styrene, methyl and dimethyl benzene. The results indicated that pH value was the most crucial factor to influence the treatment effects while reaction time and input way were considered as the importance. The removal rate for benzene could reach 60% when above 80% for methyl, and 100% for styrene and dimethyl. The variation mechanisms between chlorine dioxide, chlorite and chloride which determine the drinking water quality also discussed.

Keywords: Benzene homologous compounds; chlorine dioxide; drinking water treatment.

1 Introduction

For the drinking water treatment, the oxidation agents—chlorine, chloroform, sodium hypochlorite, chlorine dioxide, ozone, and potassium permanganate to different extent, are being used. The advantages of chlorine dioxide in pretreatment of drinking water are algicidal effect and negligible formation of halogenated by-products (Fiessinger, 1985). The main inorganic by-products in the utilization of chlorine dioxide are chlorite and chlorate which are reported to be toxic for causing methemoglobinemia if in high concentration. The costs for applying ClO_2 with chemical methods such as the reaction between sodium chlorite and hydrochloric acid are so expensive and causes a potential obstacle for the substitution of chlo-

rine by chlorine dioxide in the near future except for an application of the economical method. The aim of this paper is to evaluate the possibilities of cleaning up the benzene homologous group from a severely contaminated karst aquifer, which is a project of a large remediation program in situ funded by the Scientific and Technology Commission of China. The organic compounds with high concentrations leached into the aquifer through leakage of oil tanks and wastewater discharge pipes at the research site, so the chlorine dioxide treatment technique was taken for accelerating decomposition of the organic matters.

2 Characteristics and advantages of composite generator

The generating principles of chlorine dioxide composite disinfectant generator (CDCDG) are as follows, NaCl solution is electrolyzed to produce mixing gases which are mainly composed of ClO_2 , Cl_2 , and little amount of O_3 and H_2O_2 , but chlorine dioxide occupies more than 70% by evaluation with the corresponding total available chlorine. The simple structure of CDCDG is diagramed in Fig. 1.

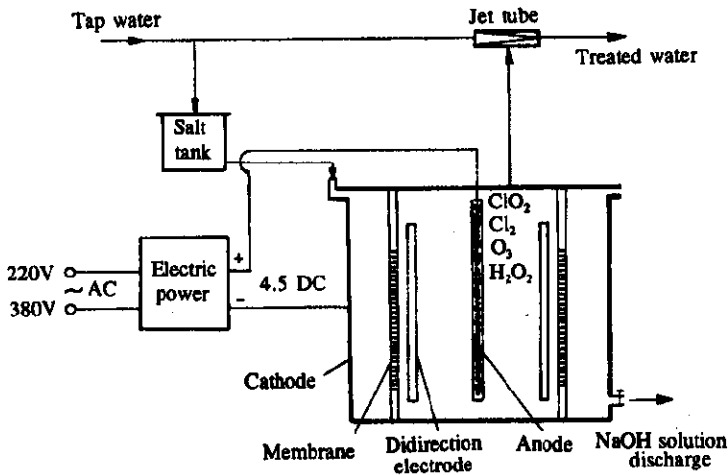
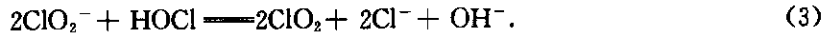
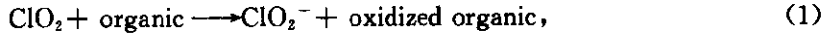


Fig. 1 Illustration of structure of chlorine dioxide composite generator

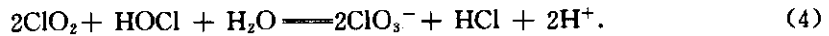
A lot of advantages of CDCDG make it serviceable in environmental activities in China now. Only ordinary salt is used as raw material. Its electrolysis has rational structure without the need of cooling. With the electrolysis voltage of 4.5 V, it obviously can save energy. The produced mixing disinfectants have powerful sterilization effects when it can diminish and decompose existing carcinogen compounds which usually are produced in drinking water by using chlorine and sodium hydrochloride. In practice, the mixing disinfectants are injected directly into water line or network, and the generators are widely employed in water treatment, clinic usage and food industry and so on in China.

3 Reaction mechanisms of oxidants

In the electrolysis process of salt, the mixing gases of ClO_2 , Cl_2 , O_3 and H_2O_2 are produced. As the relevant reactions with water molecules and organic micropollutants, hydrochlorous acid is formed by chlorine, in addition, chlorite and chlorate ions are resulted from chlorine dioxide, in which the redox reactions are recycled, eventually approaching balance. The main reactions are recapitulated as follows :



If high level chlorine has been contained in the solution, a side reaction with chlorine dioxide occurs :



The proposed yield rate of chlorate can be described by Equation (5) :

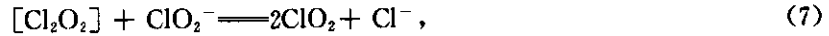
$$d[\text{ClO}_3^-]/dt = 2k[\text{ClO}_2][\text{HOCl}], \quad (5)$$

in which $k = 1.28 \text{ mol}/(\text{L} \cdot \text{min})$ at 25°C (Aieta, 1986).

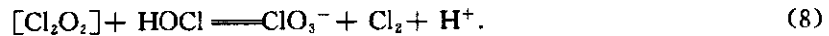
The reactions cause formation of the unsymmetrical intermediate Cl_2O_2 :



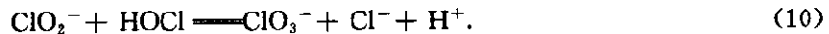
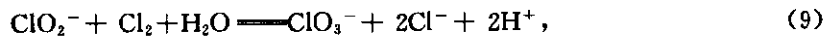
The intermediate forms very rapidly and reacts with chlorite to produce chlorine dioxide again :



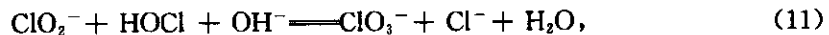
at low initial concentration or in the case of exceeding hypochlorous acid, chlorate ion could be formed by the following reaction :



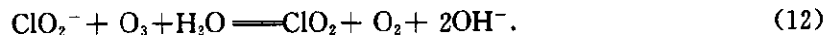
The stoichiometry of the undesirable reactions those form chlorate in low concentration of chlorite or presents of excess chlorine is given :



At alkaline conditions :



and values of pH ranges from 5 to 6 :



Typically, chlorine dioxide is used at a concentration level between 0.1 – 2.0 mg/L (Gordon, 1990), but real concern is potential health risk caused by chlorine dioxide and its metabolites and byproducts—chlorite and chlorate ions. The best ways to minimize these harmful ions are to add reductive agents, to control pH values and to incline the concentration of hydrochlorous acid.

4 Experiments

A group of device was used for the sample analysis including GR-16A Gas chromatograph with FID detector when Sunney-20 chlorine dioxide composite generator was used for producing composite gases.

A series of the experiments simulated the oxidation processes of contaminated groundwater for the restoration of a drinking water aquifer, and the high concentrations of the tested water samples almost similar to that in the aquifer. Taking the solutions of seven kinds of benzene homologous compounds to mix uniformly with 10 liters distilled water in a dark barrel, then moving 100ml of each sample to determine the initial concentration of the compounds respectively. After running the generator, the mixing solution contacted directly with the composite gas through pumping circulation, and had molar ratio of the organic compounds and composite gases (equal to available chlorine) 1 to 1-1.5. The samples of 10 ml collected at 2, 4, 6, 8, 10, 15 minutes were extracted with CS₂ for the late measurement by gas-chromatograph, and were calculated through comparison with the standard curves.

The same experiment was repeated under the indirect contacting way by which the generator only recycled distilled water and had it containing the certain quantity of available chlorine, then the composite gases solutions were added into the samples with molar ratio of 1 to 1-1.5 for the organic compounds and mixing gases. The samples were analyzed at different time as the above experiment did.

5 Results and discussion

The mixing solution of the benzene homologous compounds was kept in a dark barrel before the test, and the initial concentrations and removal rates at different time in the way of the direct contact in which the composite gases with the molar ratio of 1:1.5 to the organic compounds were directly injected in the tested solution, are listed in Table 1.

Table 1 Removal rate of benzene homologous compounds at different contacting time (at pH 7)

Compounds	Initial conc. , mg/L	Removal rate, %		
		2min	10min	15min
Benzene	41.25	14.1	41.2	60.7
Phenylmethane	31.75	17.5	54.9	86.8
Ethyl benzene	16.15	24.7	63.5	89.8
<i>P</i> -phenylmethane	10.75	25.9	84.9	100
<i>O</i> -phenylmethane	30.25	20.9	79.1	100
<i>M</i> -phenylmethane	33.20	28.6	100	100
Styrene	62.40	100	100	100

With increase of adding mixing gases proportion, for example, the molar ratio of the organic compounds and the composite gases reached 1 to 2-5, it was found that the removal rates were not obviously changed, which meant that the molar ratio of 1:1.5 for the organic compounds and mixing gases was optimal input for the treatment considering the consumption of a portion of the mixing gases to react with other contaminants originally existing in water.

Instead, in the indirect way in which the composite gases firstly were solved in a certain amount of distilled water, then the composite gases solutions were mixed with the tested organic solutions, the removal rates of the 7 compounds after 5 minutes stirring are demonstrated in Table 2. It is evident that the removal rates in indirect way were much lower than in direct way. The main reason can be ascribed to the quick disappearance of ozone and hydrogen peroxide in the indirect way before the reaction with the benzene homologous compounds, actually the combination of O_3 and H_2O_2 could show the much stronger oxidation capability than ClO_2 . In addition, the recycling water in the indirect way contained a great quantity of chlorite ion and chlorate ion in stead of chlorine dioxide that had be alternated and consumed partially already through the reactions with chlorine and hypochlorous acid, therefore, the oxidation capability of the mixing gas was significantly decreased. Explicitly, the best operation way was directly contacting the treated water in order to react with ozone, hydrogen peroxide and more chlorine dioxide.

Chlorine dioxide has very strong oxidation capability to decompose benzene ring, therefore ClO_2 as high potential to be used in water treatment. Formation of by-products during the oxidation processes is being investigated in author's research project. It can be found that styrene was much easier removed than benzene in redox conditions. The reason can be explained that the electrons in benzene ring formed an enclosing system, so density of electron cloud obviously decreased, and benzene ring hardly was oxidized through the loss of electrons. But the active radical was added into styrene ring, specially the double bond of ethylene in styrene structure formed a conjugated system with benzene ring, which enlarged the activity of styrene, therefore styrene easily lost electrons and was oxidized.

Table 2 Removal rate of benzene homologous compounds with indirect contact way (after 5 min)

Compounds	Initial conc. , mg/L	Removal rate, %
Benzene	41.25	9.5
Phenylmethane	31.75	8.3
Ethyl benzene	16.15	7.9
<i>P</i> -phenylmethane	10.75	8.2
<i>O</i> -phenylmethane	30.25	7.4
<i>M</i> -phenylmethane	33.20	7.9
Styrene	62.40	21.4

The experiment indicated that pH values significantly influenced the removal rates of the

organic compounds. Through the adjustment of pH values in the tested solutions, the removal percentages were measured after chlorine dioxide was injected into the tested solutions with molar ratio of 1:1.5 to the benzene homologous compounds in indirect contact way. The differences of removal rates are shown in Table 3. It was evidence that the decomposition results was much better in acidic conditions than in alkaline conditions because a portion of chlorine dioxide could be consumed by the disproportionation reaction at alkaline conditions, and the relative reaction can be described in Equation (11). However, the concentration in acidic conditions could keep stable, which is explained by Equation (12). The detailed study on influence of pH values to removal rates of benzene and styrene is displayed in Fig. 2.

Table 3 Removal rate of benzene homologous compounds with indirect contacting way at different pH(after 15 min)

Compounds	Initial conc. , mg/L	Removal rate, %		
		pH 5	pH 7	pH 10
Benzene	5	54.0	48.2	24.1
Phenylmethane	5	71.7	63.5	52
Ethyl benzene	5	84.2	78.7	73.5
<i>P</i> -phenylmethane	5	84.4	77.6	73.0
<i>O</i> -phenylmethane	5	84.1	80.3	73.7
<i>M</i> -phenylmethane	5	84.0	79.8	70.4
Styrene	5	100.0	98.7	90.5

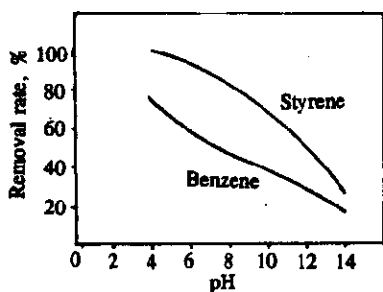


Fig. 2 Influence of pH values on removal rates of benzene and styrene treated by chlorine dioxide

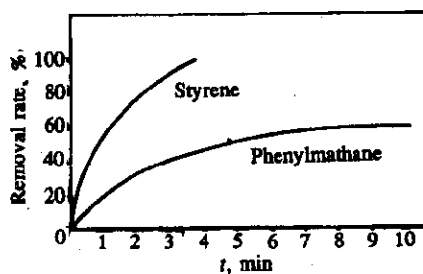


Fig. 3 Removal rate increases of phenylmethane and styrene with reaction time

It is confirmed from Table 1 that removal rate was proportional with operating time. Depending on Equation (1), chlorine dioxide, at the beginning showed that very strong oxidation capability for organic chemicals, then was reduced to be chlorite anion, so the removal rate appeared quite high for a moment. But chlorite still kept the strong oxidation to continue decomposing the organic compounds even oxidation reaction gradually became weaker and weaker with reaction time. Taking phenylmethane and styrene as the samples to test the reaction rate at pH 7, the relative removal rate of the two organic matters is shown in Fig. 3.

It can be seen that a stronger removal occurred at the beginning, then appeared stable gradually.

However, chlorine dioxide was unstable in the solution even it showed the stronger oxidation capability than chlorite and chlorate, and the later two anions also performed the manifest oxidation effects. Nevertheless, the actual concentration of chlorine dioxide was alternated by the existence of chlorine, chlorite, chlorate all of which were determined by pH value in the solution according to Equation (4), (8), (9), (10), (11), and (12), respectively. Definitely, adjustment of pH values would be the critical effect to control concentrations of chlorine dioxide, chlorite and chlorate. The later two harmful ions could be removed by treatment with a reducing agent such as sulfur dioxide-sulfite ion at pH values of 5–7 in a matter of minutes (Gordon, 1990). By using Fe(II) for elimination of chlorite from drinking water, the redox reaction was kinetically rapid over pH 5–7 as well (Iatrou, 1992).

The chlorine dioxide composite disinfectant generator is the valid and powerful equipment for water treatment, particularly, is very useful in China and other developing countries with the advantages of high cleaning effects, low cost and convenient operation, but concentration of chlorite and chlorate should be rigidly controlled in drinking water treatment.

6 Conclusions

The mixing gases produced by the chlorine dioxide composite disinfectant generator could competently oxidize and remove some benzene homologous compounds in water treatment processes. The optimum input of the mixing gases for decomposing the benzene homologous compounds was with the ratio of 1–1.5 to 1 considering the alternation and consumption of chlorine dioxide through the reactions with chlorine and hypochlorous acid in the mixing gases solution. The effective reaction must be at the condition of pH 5–7 in which the high cleaning rate could be obtained, and formation of chlorine and chlorate could be minimized. The operation should directly circulate the treated water in order to keep enough quantity of chlorine dioxide and have ozone and hydrogen peroxide reacted with the organic contaminants. The removal rate also went up with the increase of reaction time, but gradually got stable after a few minutes.

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