二氧化氯消毒时三氯甲烷形成量的研究

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摘要 研究了二氧化氯与氯消毒时三氯甲烷的形成量。结果表明，氯可与水中有机物反应形成三氯甲烷，其形成量随水中有机物含量、氯投加量，pH值的升高而升高，当COD为3 mg/L，投氧量为7 mg/L时，经48 h反应后，三氯甲烷形成量将超过国家标准规定的60 μg/L。二氧化氯不与有机物反应形成三氯甲烷。11.33 mg/L的二氧化氯与COD为2.67 mg/L的水样经48 h反应，三氯甲烷形成量低于检出限，二氧化氯与氯复配使用也可抑制三氯甲烷的生成，但二氧化氯对已形成的三氯甲烷无去除作用。

关键词 二氧化氯，三氯甲烷，消毒，消毒副产物。

饮用水传统的消毒方式是投氯。但近年来，氯消毒时产生的卤代烃(THMs)等消毒副产物引起了人们的广泛关注[1-3]。在我国，对部分省、市饮用水中挥发性卤代烃含量的调查发现，无论以地下水或地表水为水源水，经液氯消毒的自来水中均能检出卤代烃，其含量大大高于水源水[6-8]。为保证人体健康，各国纷纷制订了有关卤代烃的水质标准，我国规定饮用水中三氯甲烷含量不得超过60μg/L。

为了满足饮用水标准中对卤代烃含量的要求，国外对氯的代用物如二氧化氯，臭氧，氯胺等的研究颇为活跃，其中二氧化氯的研究与应用更是引人注目[4,5,13]。在我国，应用臭氧与氯胺消毒的研究已见诸报道[9,10]，但有关二氧化氯消毒方面的研究还不多见，笔者研究了二氧化氯的杀菌杀藻性能[11]，还研究了二氧化氯消毒时卤代烃的形成量，并与氯气进行了比较。

1 实验材料与实验方法

1.1 实验用水样

实验用水样由青岛白沙河水厂源水(引黄济青棘洪滩水库输来)与本实验室内鱼缸中水混合而成，这是因为，青岛白沙河水厂源水COD值过低，故使用鱼缸内COD值较高的水与之混合得到COD含量适宜的水样进行实验。

1.2 二氧化氯储备液

用亚氯酸钠酸化法[12]制得二氧化氯储备液，浓度约为500 mg/L，为避免其降解，低温避光处密封保存。

1.3 次氯酸钠储备液

购自青岛化工厂，浓度约为1 mol/L，实验前稀释到500 mg/L(以有效氯计)备用，二氧化氯与次氯酸钠储备液每次使用前均用碘量法[12]标定其浓度。以下所指的浓度单位，对二氧化氯是ClO_2，mg/L，对次氯酸钠是有效氯，mg/L。

1.4 实验方法

配制水样，测定其COD，pH值，装入大试剂瓶，之后加入一定量的二氧化氯或次氯酸钠，摇匀密闭，避光静置，每隔一定时间取样测定三氯甲烷含量与消毒剂残余量。

1.5 分析测试方法

实验中有关水质指标的测试均参照《生活饮用水标准检验法》(GB5750-85)以及《水和废水标准检验方法》[12]。pH：pH电极法；COD：重铬酸钾法；二氧化氯，总有效氯：碘量法；二氯甲烷：气液平衡-气相色谱法。

2 实验结果与分析

2.1 单独使用二氧化氯时三氯甲烷形成量

三氯甲烷形成量实验结果见表1。由表1

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表 1　单独使用二氧化氯时三氯甲烷形成量[1)]

接触时间(h)	0	1	3	6	11	24	30	35	47
残余 ClO_2(mg/L)	11.33	10.76	10.46	9.52	9.06	9.29	9.27	9.22	9.13
三氯甲烷(μg/L)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

1) 水中 COD=2.67 mg/L，反应温度 10±1 C

可看出，在 47 h 接触时间内，较高 COD 含量的水样(COD=2.67 mg/L)与较高浓度的二氧化氯(11.33 mg/L)相接触，也不会形成三氯甲烷。

2.2　单独使用次氯酸钠时三氯甲烷形成量

2.2.1　次氯酸钠投加量对三氯甲烷形成量影响

实验结果见图 1，由图 1 可见，随着接触时间的延长，三氯甲烷含量不断升高，这是由于有效氯与有机物反应而生成三氯甲烷。从图 1 中还可看出，次氯酸钠投加量越高，三氯甲烷形成量也就越高。

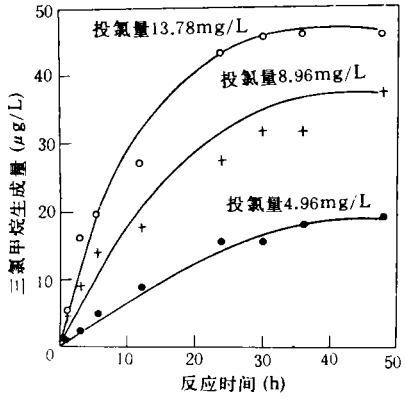

图 1　不同投氯量时三氯甲烷的形成量
反应温度 10±1 C，原水 COD2.94 mg/L

2.2.2　水中 COD 含量对三氯甲烷形成量影响

实验结果见图 2，随着接触时间的延长，三氯甲烷含量不断升高，且水中 COD 含量越高，三氯甲烷形成量也就越高。黄君礼等对腐植酸进行氯化处理时，发现三氯甲烷形成量随腐植酸含量的升高而升高，与本实验的结果相一致[9,10]。

2.2.3　pH 值对三氯甲烷形成量的影响

在含一定 COD 的水样中，加入 HCl 或 NaOH 调节水的 pH 值，然后加入一定量的次氯酸钠，隔一定时间取样测定三氯甲烷含量与消毒剂残余量。

实验结果见图 3。当 pH 从 6 升到 8 时，三氯甲烷形成量随之升高。

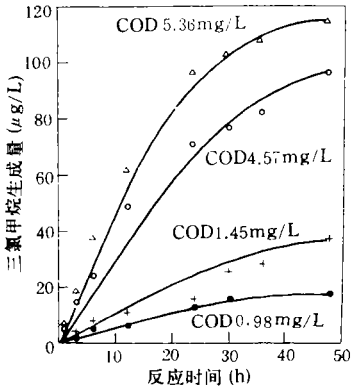

图 2　水中不同 COD 含量时三氯甲烷的形成量
反应温度 10±1 C，投氯量 8.52 mg/L

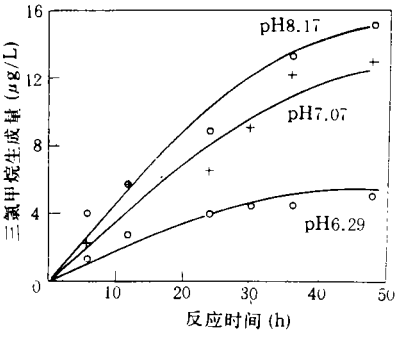

图 3　pH 值对三氯甲烷形成量的影响
反应温度 10±1℃，原水 COD1.85 mg/L，投氯量 8.50 mg/L

2.3　二氧化氯与次氯酸钠共同使用时三氯甲烷形成量

向水样中加入等量的二氧化氯与次氯酸钠，隔一定时间取样测定三氯甲烷含量与消毒剂残余量。实验结果见表 2。由表 2 可见，COD 为 0.60 mg/L，二氧化氯与次氯酸钠共同使用，投加量为总有效氯 8.7 mg/L 时，在 48 h 之内未检出三氯甲烷。这表明在消毒工艺中配合使用二氧化氯与次氯酸钠，可抑制三氯甲烷的形成。

2.4　二氧化氯对三氯甲烷的去除作用

表 2 二氧化氯与次氯酸钠共同使用时三氯甲烷的形成量(水中 COD=0.60 mg/L，反应温度 10±1℃)

接触时间(h)	0	1	3	6	24	30	35	48
总有效氯(mg/L)	8.70	7.61	7.39	6.47	4.72	4.51	4.17	3.82
三氯甲烷(μg/L)	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.

在蒸馏水中加入一定量分析纯三氯甲烷，然后加入一定量二氧化氯，摇匀密闭，在见光与避光条件下，隔一定时间取样测定三氯甲烷含量与消毒剂残余量。实验结果见表 3，无论在见光与避光条件下，即使高达 10 mg/L 的二氧化氯也无法将三氯甲烷去除。这说明若三氯甲烷已形成，则二氧化氯对其无去除作用。故若想通过应用二氧化氯消除三氯甲烷的形成，则二氧化氯必须在投氯之前投加。也就是说，在水厂进水口以二氧化氯代替氯进行预氯化；在水进入管网之前投氯，既可满足对余氯的要求，又可降低三氯甲烷的生成量，同时注意到，见光条件下，二氧化氯浓度降低较快，而在避光条件下，二氧化氯浓度的降低不大。

表 3 二氧化氯对三氯甲烷的去除作用

接触时间	二氧化氯(mg/L)		三氯甲烷(μg/L)	
(h)	见 光	避 光	见 光	避 光
0	11.40	10.85	5.1	5.1
1	10.89	10.31	5.1	5.1
3	10.37	10.25	5.1	5.1
6	9.86	10.22	5.1	5.1
12	9.36	10.27	5.1	5.1
24	8.57	10.16	5.1	5.1
30	7.66	9.86	5.1	5.1
48	7.05	9.87	5.1	5.1

2.5 讨论

通过以上实验可见，单独应用二氧化氯时，不会与有机物反应形成三氯甲烷，而应用氯时，则会与有机物反应形成三氯甲烷，且形成量随投氯量、水中 COD 含量和 pH 值的升高而升高。当水中 COD 在 3 mg/L 以上，投氯量在 7 mg/L 以上时，三氯甲烷的形成量可能超过国家标准规定的 60μg/L。应考虑采用某些技术措施以降低三氯甲烷的生成量。

关于单独使用二氧化氯及复配使用二氧化氯与氯时，可抑制三氯甲烷的形成，国外也有此类报道。如有的研究者用 4.2 mg/L 二氧化氯与 2.5 mg/L 氯复配使用，可使三氯甲烷的形成量降低 84%[5]。据认为这是由于二氧化氯优先与水中的有机物反应，从而抑制了它们与氯作用形成三氯甲烷。从本研究看，虽然单独使用二氧化氯及复配使用二氧化氯与氯时，未检出三氯甲烷，但明显可见消毒剂浓度的降低，这意味着消毒剂与有机物反应而被消耗，对于其反应产物及反应途径，对特定水质二氧化氯与氯的最佳配比，应做进一步的研究。

关于应用二氧化氯消毒时成本概算，国内目前尚无这方面运行经验可供参考。据美国环保局在南加州 Chester 城的生产性实验，改用二氧化氯代替氯进行处理，氯的使用量降低了，若仅用氯气，投加量为 11 mg/L，改用二氧化氯后，氯的使用量降为 3.6 mg/L。这大大抵消了使用二氧化氯所致的成本升高。从总的概算来看，改用二氧化氯之后，总制水成本升高了 1.27%[13]。

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tive to acid deposition in this country.

Key words: sulfate ions, soils, adsorption capacity, aquatic ecosystems.

Method for Testing the Photodegradability of Herbicides Adsorbed on HPTLC Plates. Yue Yongde (Dept. of Environ. Protection, Anhui Agriculture University, Hefei 230036): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 16—18

A rapid and effective method to detect the photodegradability of herbicides in an adsorption state was developed with a high performance thin layer chromatography (HPTLC) technique. Two herbicides, chlortoluron and fluorodifen, were applied directly on a silica gel 60 F254 high performance thin layer plate (10X20cm) by Linomat Ⅳ in a dosage of 400—800 ng per slit, then irradiated under natural sunlight, and then the HPTLC plates were developed and measured with a DESAGA 60 Scanner. The photolytical dynamics of chlortoluron and fluorodifen, the optimal dosage and other test conditions were also described in this paper.

Key words: herbicides, high performance thin layer chromatography (HPTLC), chlortoluron, fluorodifen.

Treatment of Zn^{2+} Contaminated Wastewater with a Method of Sulfate Bio-reduction. Ma Xaohang et al. (Zhejiang Institute of Microbiology, Hangzhou 310012): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 19—21

A process for the treatment of Zn^{2+} containing wastewater by sulfate-reducing bacteria in an upflow anaerobic sludge bed reactor has been studied. When the concentrations of COD and Zn^{2+} in influent were 320 mg/L and 100 mg/L, respectively, the reactor could be successfully operated. Under this condition the removal rates of COD and Zn^{2+} were 73.8% and 99.8% respectively. When the concentration of Zn^{2+} was less than 500 mg/L the reactor was operated successfully. Whereas when the Zn^{2+} concentration in influent was higher than 500 mg/L the activity of the sulfate-reducing bacteria was suppressed by Zn^{2+}. When the Zn^{2+} concentration was 500 mg/L and the retention time was 9 h, the reactor had a volume removal rate of Zn^{2+} reaching as high as 1329 mg/(L • d).

Key words: sulfate reducing bacteria; heavy metal wastewater; upflow anaerobic sludge bed reactor.

Study on the Characteristics of a New Class of Double Hydroxyl Stratified Clay Materials for Removing SO_2 from Flue Gas. Chen Yinfei et al. (Zhejiang University of Technology, Hangzhou 310014): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 22—25

An experimental study was conducted on the desulfurization characteristics of a synthesized class of double hydroxyl stratified clays as a desulfurizer of high temperature flue gases. The results show that after roasted at a high temperature the materials had a higher capacity of desulfurization, a higher rate of SO_2 adsorption, and a higher selectivity to SO_2. By studying the reaction rates at different temperatures, the optimum temperature for each of the stratified double hydroxides (SDH) was found to be 700℃ for NiAl SDH and 750℃ for both ZnAl SDH and ZnMgAl SDH. The selectivity to SO_2 was found to increase with the temperature rising from 500℃ to 750℃. During the first 10 minutes after a regeneration, the SDHs had essentially an unchanged reaction rate and an insignificantly decreased capacity of desulfurization.

Key words: clay, stratified double hydroxides, desulfurization, SO_2, flue gas.

BOD/DO Mathematic Models for the Water Quality of Lake Moshuihu in Wuhan City and Their Parameters Identification. Mao Rongsheng et al. (Dept. of Rivers, Wuhan University of Hydraulic and Electric Engineering, Wuhan 430072): *Chin. J. Environ, Sci.*, **16**(4), 1995, pp. 26—31

In terms of hydrology, water quality and topography, the Moshuihu Lake in Wuhan City was zoned into five sub-lake areas, for each of which a BOD/DO mathematic model of a scatter structure was set up, together with a method developed for identifying the parameters of the models. The simulation study and model testing gave satisfactory results. Systematology and microcomputerized programming operation were applies as an analysis was made. The developed models were found to meet the needs for planning and managing the water quality of the lake.

Key words: lake, water quality, BOD/DO model, parameters identification, simulation.

Formation of Chloroform during Water Disinfection with Chlorine Dioxide. Wang Yongyi et al. (Dept. of Environ. Eng., Qingdao College of Architecture and Construction Engineering, Qingdao 266033): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 32—34

The results show that chlorine reacts with organic

matter to form chloroform, the production of which increases with an increase in COD, pH, and chlorine dosage. The level of chloroform would exceed the national drinking water quality standard (60 μg/L), 48 hours after dosing 7 mg/L chlorine to water with a COD of 3 mg/L chlorine dioxide does not react with organic matter to form chloroform. After adding 11.33 mg/L of chlorine dioxide to a water having a COD of 2.67 mg/L for 48 hours, the level of chloroform was below detection limit. Moreover, a combined use of chlorine dioxide and chlorine can inhibit the formation of chloroform. However, chlorine dioxide was not able to remove chloroform already present in water.

Key words: chlorine dioxide, water disinfection, chloroform.

Study on the Degradation of DNA in an Acidic Medium by HPLC Using Gradient Elution. Long Yaotin et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 35—38

The determination and separation of bases from the degradation products of DNA in hydrochloric acid, perchloric acid, trichloroacetic acid, trifluoroacetic acid and formic acid were described. The hydrolysis yields of DNA adduct products of MNU also were presented. The effects of mobile phase composition, flow rate, column temperature, gradient ramp, pH value, salt concentration, and buffer concentration on capacity factors (K') were respectively discussed. The experimental results showed that hydrochloric acid is a favorable hydrolytical medium for DNA degradation and high recovery of DNA bases can be obtained. The optimum hydrolytical conditions for adduct products of DNA of MNU were 1 mol/L hydrochloric acid, 20 min, and 80—100℃.

Key words: HPLC, DNA, MNU, adduct.

A Study on Technology for Solidification of Pulverized-Coal Ash and Its Application. Guo Qingyun (Nanjing Institute of Environmental Protection Science for Electric Power, Ministry of Electricity Industry. Nanjing 210031): *Chin. J. Environ. Sci.*, **16**(4) 1995, pp. 39—41

Test and research have been made on a solidification technology for pulverized ash to be used in suppressing dust of ash ponds or landfills for coal-fired power plants. As a result, two series of ash-stabilizing agent have been already developed. The solidified ash has a compressive strength over 16 kg/cm^2, with a maximum of 70 kg/cm^2, and stability coefficients in water and in freezing state are over 0.90 and even up to 1.00. This process is highly efficient in dust suppression, durable in operation, low in cost, abundant in raw material supply, simple in application, and easy in popularization. It can be used for ash ponds or landfills in operation or being full, for reinforcing ash dykes and for preventing permeation of ash ponds.

Key words: solidification technology, pulverized-coal ash, stabilizing agent, stability coefficients.

Preliminary Study on the Biological Effects of Lignin Dressing Seed on Plant Growth. Fan Xiuying et al. (EIA Unit, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 42—45

Lignin, extracted from the black liquor discharged from small and medium-sized pulp and paper mills, was used as a seed dressing agent to coat seeds at a rate of 0.4% by weight of seed and at pH 7.8, and the dressed seeds were grown in experimental plots containing a sand and soil culture and in fields. The results show that the seed dressing increased the rate of seed germination, accelerated the development of root systems, enhanced the effective tillering of wheat, increased the resistance to drought and to pests, the number of seeds in a single ear, and the weight per thousand seeds, and thus raised the yield. The treated wheat and maize grown in all experimental fields in Shandong and Hebei provinces and in Beijing were found to have an over 10% increase in yield as compared to control. The biological effects of seed dressing were found to be closely related to the process of extracting lignin from black liquor, the source of pulping raw materials, the rate of dressing agent used, the pH value of dressing solution, the variety of crops and the fertility of soil. The cost of lignin as a seed dressing agent is low due to its being from pulping waste and the dressing technology is quite simple, environmentally sound and easy to be diffused for agricultural purpose.

Key words: lignin, pulping waste, waste recycle, seed dressing agent, wheat, maize.

Development of A Concrete Water-Reducing Admixture Using Lignin from Alkaline Wheat Straw Pulping Black Liquor. Fan Yaopo et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(4), 1995,