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KINETIC MODEL FOR CHLORINE DECAY AND DISINFECTION BY-PRODUCTS FORMATION USING ABTS METHOD AND DPD METHOD

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ABSTRACT. The kinetics of chlorine decay of the pre-treated water collected once a month from the Gilau Water Treatment Plant after one of the sand filters was investigated. The chlorine species reacts with ABTS (2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonicacid-diamonium salt) to yield a green colour product that is measured at 405 nm wavelength with a spectrophotometer. The second method used for the investigation of chlorine consumption was by means of DPD (N,N-diethyl-p-phenylenediamine), where chlorine oxidizes DPD which takes on a red colour. The absorption is measured with a spectrophotometer at a wavelength of 515 nm. Both methods are useful for the determination of chlorine consumption in the treated water from distribution systems.

Keywords: Disinfection by-products, ABTS method, Chlorine consumption, THM formation.

INTRODUCTION

Chlorine is mostly used in water treatment plants from Romania for water disinfection. The regulation and monitoring of disinfection by-products has become a current issue after Romania's entry to the UE and after many previous studies have shown the possible adverse health effects on humans of this compounds [1, 2]. Their formation in treated water depends by the type of disinfection process and the type of disinfectant agent that is used.

Chlorine's popularity is not only due to lower cost, but also to its higher oxidizing potential which provides a minimum level of residual chlorine throughout the distribution systems and protects against microbial recontamination [2, 3]. For that, over of many years, chlorine became the most popular disinfecting agent due to its ability to kill most pathogens. In 1974 was finding that after adding of chlorine to water in order to disinfect it, this resulted the formation of compounds such as chloroform (one of the component of trihalomethanes class) due to

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reaction of chlorine with the organics present in the water. After then hundreds of additional disinfection by-products have been identified including haloacetic acids and haloacetonitriles [4, 5]

Trihalomethanes (THMs) is the class of disinfection by-products that are most identified in treated water. Usually chloroform is the most commonly THMs compound in drinking water and it is present in the highest concentration.

Many parameters have an important influence on the formation of THMs. Previous research studies have shown that the major variables that affect THM formation are chlorine dose, concentration and nature of natural organic matter, contact time, pH, temperature of water and the presence of inorganic ions like bromide [3, 4].

The major factor that influence the THMs formation is the organic matter present in water supplies, they reacts with chlorine and leads to the formation of THMs. The type and characteristics of organic precursors directly affect the formation of THMs. Naturally occurring humic and fulvic substances which constitute a large fraction of the organic matter in water are the major THMs precursors [6]. Increase of chlorine dose has been reported to have positive influence of disinfection by-products yield. The same is true for increased concentrations of natural organic matter and increased temperature. The presence of bromine ions shifts the speciation of disinfection by-products to more brominated analogues, while increased pH can enhance the formation of some categories of disinfection by-products, ex. THMs and inhibits the formation of some others, ex. haloacetonitriles and haloketones [3]. Higher THM concentrations are expected at higher levels of the above mentioned parameters [7,8].

RESULTS AND DISCUSSION

Total chlorine (including all species: $HOCl$, NH_2Cl, ClO_2 and ClO_2^- react rapidlly with ABTS or DPD and it is impossible to have a distinction between the different species (relations 1, 2):

$$ClO_2 + ABTS + 2\,H^+ \rightarrow ClO^- + ABTS^+ \tag{1}$$

$$ClO_2^- + 4\,ABTS + 4\,H^+ \rightarrow Cl^- + 4\,ABTS^+ + 2\,H_2O \tag{2}$$

To determine NH_2Cl both HOCl and ClO_2 are destroyed by the addition of nitrite prior to ABTS addition. Nitrite rapidly reacts with ClO_2 and HOCl but only slowly with NH_2Cl. Nitrite does not react with ABTS and does not interfere in the determination of NH_2Cl fraction [6, 7, 8]. Four minutes are sufficient for a complete destruction of ClO_2 and HOCl. The concentration of free chlorine is calculated by subtracting monochloramine from total available chlorine fraction. Table 1. shows the concentration ($mg\cdot L^{-1}$) obtained for total chlorine, free chlorine and NH_2Cl in laboratory kinetic experiments with both methods: ABTS and DPD.

It is observed a slightly small difference between the results.

Table 1. Comparison between results obtained with ABTS and DPD method for determination of total chlorine, free chlorine and NH_2Cl.

Time (minutes)	**ABTS method**			**DPD method**		
	Total chlorine (mg/l)	**Free chlorine (mg/l)**	**NH_2Cl (mg/l)**	**Total chlorine (mg/l)**	**Free chlorine (mg/l)**	**NH_2Cl (mg/l)**
0.333	1.62	1.6	0.03	1.73	1.68	0.04
0.666	1.32	1.2	0.06	1.35	1.26	0.08
1	1.26	1.2	0.07	1.29	1.24	0.10
3	1.1	1	0.07	1.14	1. 7	0.11
6	0.92	0.8	0.12	0.98	0.84	0.15
15	0.81	0.5	0.21	0.85	0.67	0.28
40	0.7	0.4	0.21	0.74	0.55	0.23
60	0.62	0.36	0.17	0.68	0.39	0.19
90	0.56	0.3	0.17	0.60	0.37	0.17
120	0.52	0.3	0.17	0.54	0.34	0.16
240	0.46	0.28	0.14	0.48	0.29	0.13
600	0.26	0.2	0.08	0.29	0.22	0.06
690	0.19	0.14	0.06	0.23	0.18	0.05
780	0.12	0.1	0.04	0.15	0.13	0.04

The advantages of these methods are:

- they are easy to use and can determine with a high precision the total chlorine, free chlorine and NH_2Cl concentration.
- can help us to try to predict the potential formation of chlorination by-products, such as trihalomethanes – see figure 1.
- help in the prediction of chloroform formation in the distribution system if we respect the water condition (Chlorine dose, pH, temperature).

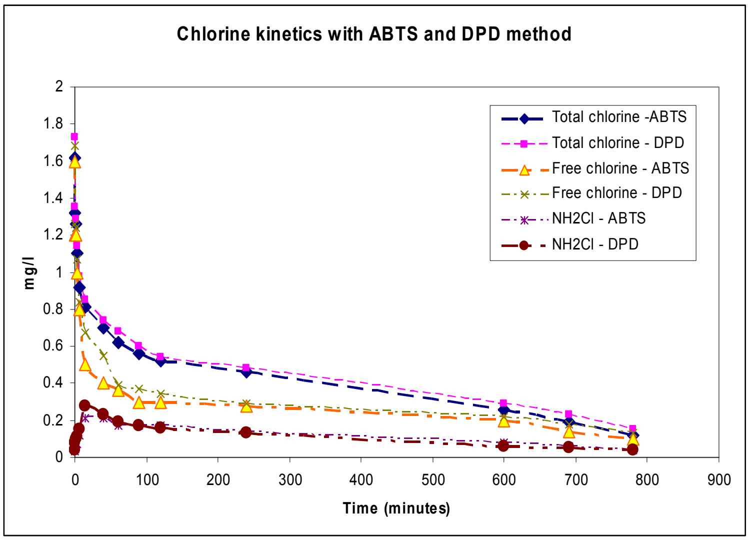

Figure 1. Total Cl_2 and NH_2Cl concentration vs. reaction time for both methods (ABTS and DPD).

In figure 2.a., is shown the result of chlorine kinetics experiment in laboratory and in figure 1.b., is shown the chloroform kinetics formation obtained from chlorine kinetics experiment. At each desired reaction time, in the water sample was injected thiosulfate solution to quench chlorine and stop the THM formation.

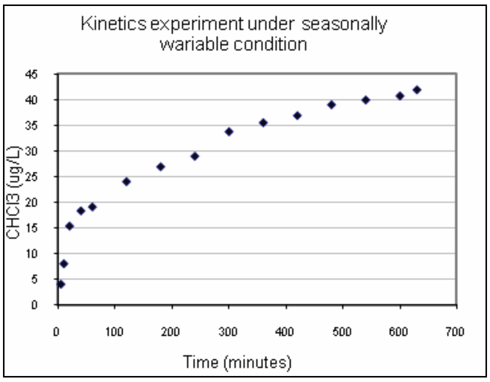

Figure 2.a.: represent the chlorine kinetics experiment (total chlorine kinetics, free chlorine and NH_2Cl kinetics.

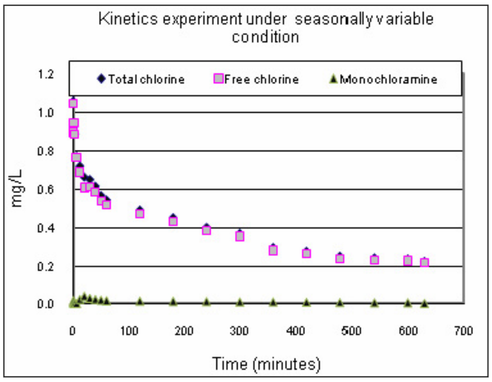

Figure 2.b.: Show the chloroform formation kinetics from experiments.

To assess the possibility to simulate the THM formation in the distribution system, $CHCl_3$ formed in laboratory experiments was compared with $CHCl_3$ concentration measured in the distribution system on the sampling day – see table 2.

Table 2. Chloroform formation in laboratory experiment and the chloroform value measured in the sampling point.

Sampling point	Chloroform concentration ($\mu g \cdot L^{-1}$) in water sample taken from Gilau Water Treatment Plant – Cluj (a) and chloroform ($\mu g \cdot L^{-1}$) concentration obtained in laboratory experiment (b) for different month									
	1a	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
A	0.6		0		0		0		0	
B	4.9	2.1	0	0	0	0	0	0	0	0
C	12.4	13.2	8.4	7.8	2.22	3.8	8.09	7.9	8.22	7.9
D	18.7	19.1	47.7	50.1	9.34	11.0	16.71	15.98	20.81	21.14
E	28.4	29.6	47.0	49.3	6.36	7.8	18.70	19.03	29.26	30.06
F	35.2	36.6	66.9	70.4	27.77	26.8	18.99	19.8	27.12	28.24
G	37.1	38.3	66.6	69.3	21.08	20.9	20.90	21.14	32.41	33.56
H	23.2	24.8	71.1	72.8	28.17	29.3	21.60	22.05	33.86	34.09

The sampling was started from Gilau water treatment plant to distribution system in Cluj Napoca (A – raw water, B – filtrated water, C – exit reservoir, D – Sapca Verde, E – Beer factory, F – Chemistry faculty, G – Environmental science faculty, H – Institute of public health) in different month (1a –$CHCl_3$ concentration in July in the water take from sampling point, 1b – $CHCl_3$ concentration in July in laboratory kinetics experiment which correspond in time with the water that arrived to the sampling point; the same is for 2a and 2b but for September water sample; 3a, 3b – December; 4a, 4b – March; 5a, 5b - May).

CONCLUSIONS

Both colorimetric methods are easy to use and give precise results. The difference between the two different methods was very small (3 %). The difference between ABTS and DPD method is, ABTS method is easier to apply in comparison with DPD for a long experiment like a kinetics experiment.

The two methods give really information between the chlorine consumption and the $CHCl_3$ formation. That helps us in the future to make the prediction of total THMs formation. The results of measured THMs show that $CHCl_3$ is the main THMs formed in distribution system and its amount is in the range 0.6 – 73 $\mu g \cdot L^{-1}$, value that is under the maximum permissible level according to the EU drinking water safety regulation.

EXPERIMENTAL SECTION

Sampling: Pre-treated water was collected at the treatment plant after one of the sand filters once a month and stored in 5 L plastic bottles at 4 ^0C until the chlorination experiments. pH and water temperature were measured at the sampling site when the sample were taken.

Reagents: $NaNO_2$, NaB_7O_5 and $Na_2S_2O_3$ were purchased from Reactivul Bucuresti (Bucharest, Romania). KI (purissim p.a.) was purchased from Merk (Darmstadt, Germany). NaH_2PO_4 used was from BPH Chemicals (Poole, England). ABTS (2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonicacid-diamonium salt) was purchased from Fluka (Buchs, Switzerland). DPD (N,N-diethyl-p-phenylenediamine) was taking from Merk (Darmstadt, Germany). Aqueous chlorine dilution was prepared from a chlorine solution for cleaning purposes (2-5 %, Sun Industries, Ilfov, Romania). NaOH, H_2SO_4 and KIO_3 were purchased from Fluka (Buchs, Switzerland).

Chlorine experiments: The chlorine dose in the water treatment plant from Gilau (where was collected the filtrated water) is regulated manually to achieve a free chlorine concentration at the exit reservoir (where the water arrives approximately 15 minutes after chlorination) of 0.5 – 0.7 $mg \cdot L^{-1}$ Cl_2 in winter and 0.7 – 0.9 $mg \cdot L^{-1}$ Cl_2 in summer. Chlorination experiments were carried out monthly with raw water collected at the treatment plant after one of the sand filters. To assess the influence of the seasonal variances in the water matrix, kinetic experiments with filtrated water will be performed monthly under the two conditions.

The experiments were conducted under two conditions:

- *Base line conditions* (pH 7, 21^{0}C, 2.5 mg/l Cl_2) to gain information about the change of the organic matter in the raw water, and seasonally variable conditions to simulate the actual process at the treatment plant.
- Experiments under *seasonally variable conditions* were carried out with pH and temperature as measured in the pretreated water on the sampling day and an initial chlorine dose according to a free chlorine concentration after 15 minutes as prescribed in the guidelines of the water treatment plant.

The chlorine concentration was determined by the ABTS method at a wavelength of 405 nm and ε has a value of 28 500 M^{-1} cm^{-1} (see figure 3.a.), and also with DPD method at a wavelength of 515 nm (see figure 3.b.). In laboratory experiment the chlorine dose added to filtrate water was the same that in the sampling day, also the temperature and the pH. The kinetics experiment time was 13 hour (is the time for the water to arrive from Gilau water treatment plant to the centre of city). The THM samples taken from kinetics experiment were preserved with sodium thiosulfate. The experiment results in the first one will give information about the seasonal variance of NOM and its influence on the THM formation potential, while the second one is an attempt to simulate the conditions at the WTP which will give information about the actual process.

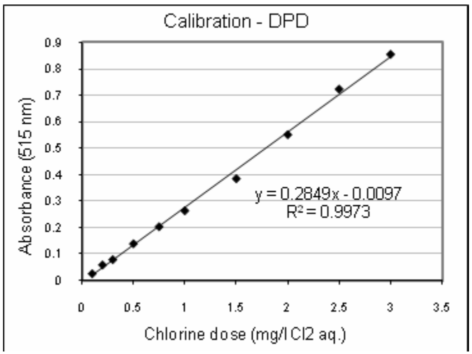

Figure 3.a.: Present the calibration curve of Cl_2 with DPD method.

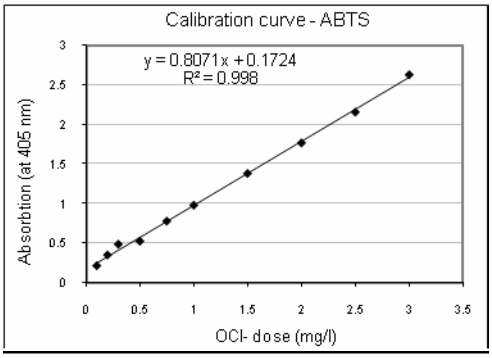

Figure 3.b.: Represent the calibration curve of OCl^- with ABTS method.

Monochloramine, total and free chlorine are measured with the ABTS method. Monochloramine and HOCl react with ABTS to a green coloured product, which can be measured at a wavelength of 405 nm.

Instrumental measurements: For the *kinetic studies* chlorine was measured colorimetrically according to standard method 8021 DPD method (powder pillow) for free chlorine determination and standard method 8167 DPD method (powder pillows) for total chlorine determination using a Hach Dr 2800 analyzer. A 25-ml cell was filled with samples and added DPD free chlorine reagent (powder pillow). After mixing, chlorine was read at a wavelength of 530 nm wavelength. Also, the chlorine concentration was determined by the ABTS method at a wavelength of 405 nm with a molar absorption coefficient ε of 28 500 M^{-1} cm^{-1}. Monochloramine, total and free chlorine are measured with the ABTS method. Monochloramine and HOCl react with ABTS to a green coloured product, which can be measured at a wavelength of 405 nm.

Trihalomethanes analysis: THMs were measured by a Thermo Finningan U.S. Trace GC Ultra gas chromatography system with an electron capture detector (GC-ECD) equipped with a TriPlus HS auto sampler. The analysis was made using headspace technique. 10 ml of sample was filled into 20 ml headspace vials and closed with Teflon lined screw caps. After that, the samples were equilibrated in an oven at 60^0C for 45 minutes. 1 ml of the headspace was then injected into the GC (Cyanopropylphenyl Polysiloxane column, 30 m x 53 mm, 3 μm film thickness, Thermo Finnigan, USA). The column program was 35^0C (hold time 3 minutes), 15^0C/minutes to 200^0C (hold time 3 minutes).

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