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DBPs CONTROL IN EUROPEAN DRINKING WATER TREATMENT PLANTS USING CHLORINE DIOXIDE: TWO CASE STUDIES

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Abstract. The paper reports results of the experiments carried out at Fortore (Foggia, South Italy) and Mosina (Poznan, Poland) drinking water treatment plants aimed at DBPs control. Pilot scale GAC filters were installed in both plants in order to assess the efficacy of different kind of GAC for chlorites, NOM and THMs removal. Both pilot plants operated with and without chlorine dioxide pre-disinfection. In Fortore plant, because of free chlorine was added in ClO_2 pre-disinfection solution, THMs formation was evaluated. Results showed an high efficacy of chlorites removal on GAC filters up to 5500 and 10000 bed volumes for mineral and vegetal GAC in Fortore and up to 11000 bed volumes in Mosina. A preliminary characterization of natural organic matter (NOM) dissolved in Fortore raw water was performed as well, in order to confirm its reactivity towards chlorine dioxide. The presence of small molecules (< 500 Da) in Fortore pre-disinfected water, has resulted in THMs and carboxylic acids formation due a fast reaction with Cl_2-ClO_2. GAC columns have shown percentages of removal ranging from 60 to 72% for THMs and ranging from 14.6 to 43% for TOC, so that adsorption represents an essential step for DBPs control.

Keywords: chlorine dioxide, chlorites, granular activated carbons; NOM, THMs.

1. Introduction

Disinfection of water with chlorine leads to the formation of unwanted disinfection by-products (DBPs), i.e. trihalomethanes (THMs), haloacetic acids (HAAs) and organohalogens. To meet new regulations, water utilities are obliged to apply improved water treatment technologies to reduce DBPs formation (Volk *et al.* 2002; Mažeikienė *et al.* 2008). In the last two decades chlorine dioxide was investigated as one of the promising disinfectants to substitute chlorine. Chlorine dioxide, as ozone, is a very strong disinfectant, efficient in killing bacteria and especially successful in deactivating viruses (Weber and Smith 1986; Abbt-Braun *et al.* 1994; Narkis *et al.* 1995; Minear and Amy 1996; Li *et al.* 1996; Junli *et al.* 1997; Korn *et al.* 2002). ClO_2 works as an oxidating but not a chlorinating agent, and thus should not form trihalomethanes (THMs) during water treatment (Lefebvre and Deguin 1996; Chang *et al.* 2000; Minear and Amy 1996; Narkis *et al.* 1995; Li *et al.* 1996; Korn *et al.* 2002) and also reduces the concentration of the precursors of organo-halogenated compounds (Karpel vel Leitner *et al.* 1996). The disadvantage of ClO_2 application is the formation of undesired and regulated inorganic by-products: chlorite (ClO_2^-) and chlorate (ClO_3^-) ions. They are harmful and may cause blood-related problems (haemolytic anaemia). The maximum contaminant level (MCL) for chlorite in drinking water is regulated, however there are considerable differences between particular MCLs (USEPA 1.0 mg/L, WHO 0,7 mg/L, Italy 0.7 mg/L, Germany and Poland 0.2 mg/L). However, most of water treatment plants that use chlorine dioxide exceed these rigorous limitations (Aggazzotti *et al.* 2004).

Chlorite ions are mainly formed during NOM oxidation, though it is also a product of a complex mechanism of the decomposition of ClO_2 in water. Usually, 1 mg of applied chlorine dioxide produces about 0.5–0.8 mg chlorites and a different (usually lower) amount of chlorates (Andrews *et al.* 1996; Weinberg, Glaze 1996; Minear and Amy 1996; Narkis *et al.* 1995; Schmidt *et al.* 2000; Korn *et al.* 2002). Taking into consideration the advantages of using ClO_2 as a disinfectant, particularly in large drinking water plants, it is desirable to efficiently remove its undesired by-products. Elimination of chlorites and chlorates by a further reduction to harmless chloride ions could greatly enhance the potential for ClO_2 usage in drinking water treatment, and lower the limitation imposed by the regulations. To lower undesirable by-products concentration in drinking water it is necessary to decrease the amount of chlorine dioxide used for disinfection, i.e. to decrease the ClO_2 demand of water. The oxidant demand of treated water is mainly caused by natural organic matter (NOM). Thus, effective NOM removal from water during the water treatment is therefore of great importance for decreasing its ClO_2 demand. According to Świetlik *et al.* (2002, 2003) the application of ClO_2 as a pre-oxidant followed by GAC filtration is efficient for the removal of NOM. The reduction of NOM amount in water reduces the disinfection by-products (DBPs) formation as well (Schmidt *et al.* 2000). Furthermore, it was reported that application of PAC or GAC filtration efficiently removes chlorites (Dietrich *et al.* 1992; Faust and Aly 1999; Karpel vel Leitner *et al.* 1996; Świetlik *et al.* 2002, 2003). As stated by Karpel vel Leitner *et al.* (1996), Faust and Aly (1999); Collivignarelli *et al.* (2002) the removal efficiency of chlorite ions on GAC was quite high and ranging from 80 to 130 mg ClO_2^-/g GAC.

The purpose of the presented study was to evaluate the efficiency of chlorine dioxide pre-disinfection followed by GAC filtration in the removal of DBPs precursors from water and to control DBPs formation. Results of pilot-scale experiments performed in two large water treatment plants: Mosina Water Treatment Plant located near Poznań (Poland) and Fortore Water Treatment Plant (South Italy) were compared in order to assess suitability of GAC for chlorites removal from water as stated by National European Directives.

In Fortore plant free chlorine (0.1 mg/L) was added to ClO2 in the predisinfection step so that THMs formation has been controlled and evaluated. The main objectives of this paper are:

- to assess the effectiveness of removing chlorites by GAC;
- to evaluate the interference of NOM in pre-disinfection and GAC processes;
- to study the efficiency of TOC and THMs removal as a function of GAC bed volumes.

2. Materials and Methods

Fortore Drinking Water Treatment Plant and pilot plant

Fortore Drinking Water Treatment Plant (Fortore, Italy) is managed by the Acquedotto Pugliese (AqP), one of the largest water companies in Europe. Fortore plant is supplied by surface water from Fortore river (South East of Italy). Raw water is influenced by non point source pollution, mostly nitrates from agricultural cultivations. The composition of raw water does not differ very much in the time.

The full efficiency of Fortore is roughly 200.000 m^3/d supplying approx. 650.000 people with drinking water.

In a treatment train raw water is pre-disinfected with chlorine dioxide, clarified by three “accelator” Degremont clarifiers and filtered through ten sand gravity filters.

Filtration is operated on sand filter beds where flow has a filtration velocity of 10 m/h and an automatic control of outflow; backwashing provide filtration to remove excessive turbidity.

After the sand filtration the water is post-disinfected with a mixture of ClO_2 and Cl_2.

The pilot plant (Figs. 1a, 1b) located at Fortore Drinking Water Treatments Plant consist of two granular activated carbon (GAC) filters (2 m high and 27 cm I.D.), working with a downstream flow of 10 m/h (M and V filters in Fig. 1a). A by-pass was created after sand filtration to supply the pilot plant (Fig. 1b) only for experiments purposes. Two different types of Camel GAC were used: one of vegetal origin (V) and the second one of mineral origin (M).

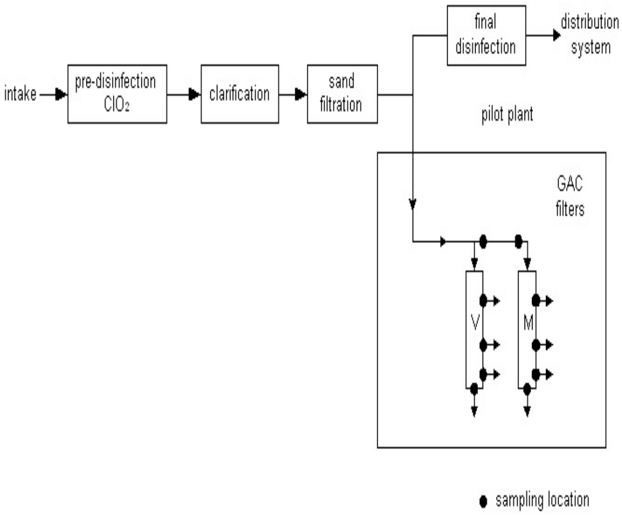

Fig. 1a. Scheme of Fortore Drinking Water Treatments Plant

Fig. 1b. Fortore GAC pilot plant

Mosina Water Treatment Plant and pilot plant

Mosina Water Treatment Plant (Aquanet Co, Poznań, Poland) is mostly supplied by underground water from Mosina Water Intake (MWI). The intake contains two barriers of wells located along Warta River. The water supplied by the lower barrier is influenced by infiltration water from the river, however the composition of the water from both barriers does not differ very much. The total efficiency of Mosina Water Treatment Plant is roughly 140.000 m^3/d supplying approx. 600.000 people with drinking water. Raw water is aerated and filtered through the sand filters to remove excess of iron and manganese. After filtration the water used to be disinfected with Cl_2, however the company has recently replaced Cl_2 with chlorine dioxide.

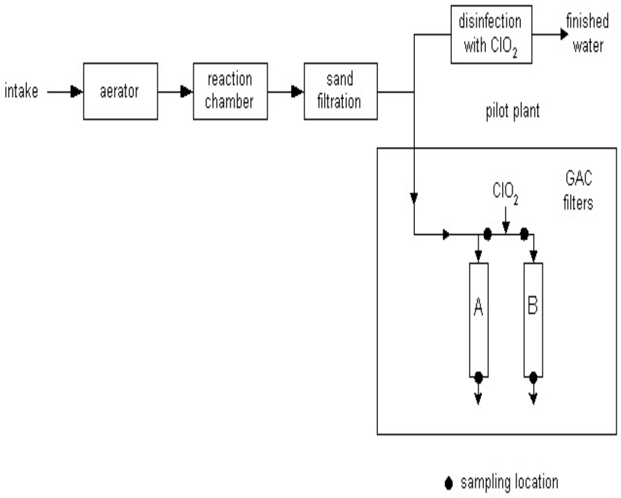

Fig. 2. Scheme of Mosina Water Treatments Plant and Mosina pilot plant

The pilot plant located at Mosina Water Treatment Plant consists of two Norit Row 0.8 Supra granular activated carbon (GAC) filters (2 m high and 7 cm I.D), working with a downstream flow of 8 m/h (A and B filters in Fig. 2).

Monitored parameters – Mosina

Chlorine dioxide demand was determined by a photometric method with N,N-diethyl-1,4-phenylenediammonium-sulfate (DPD). Absorbance was measured with a HACH DR/4000 UV/VIS spectrophotometer at 515 nm, in 1-in glass cell. The by-products: chlorites and chlorates were determined by ion chromatography with a DIONEX DX-500 system with IonPac AS-9-HC analytical column (4×250 mm) and IonPac AG-9-HC guard column (4×50 mm) connected with conductivity detector CD-20 (Dionex, USA). Total organic carbon (TOC) was analysed by LABTOC system (Pollution and Process Monitoring Ltd., England) TOC analyser using the method of sodium peroxydisulphate/orthophosphoric acid wet oxidation and UV radiation.

Chromatographic characterization and MWD of NOM was determined by HP-SEC with UV-detection at 254 and 220 nm (AD 25 detector, Dionex, USA) on a DIONEX DX-500 Chromatography System with TosoHaas TSK gel G3000 SWXL column and TosoHaas TSK gel SW guard column (Tosoh Corporation, Japan).

The eluent was a 0.01 M phosphate buffer, pH 7.00±0.05, while the samples were injected after filtration through 0.45 μm membrane filters without the addition of buffer.

Monitored parameters – Fortore

Sampling and testing protocols were as described in the Standard Methods for the Examination of Water and Wastewater (APHA … 2005) unless otherwise specified. Samples for chemical analyses were collected in acid-washed containers. Chlorine residuals were measured by the N,N-diethylp-phenylene diamine (DPD) colorimetric method. Chlorite and chlorate were measured according to the U.S. Environmental Protection Agency (USEPA) Method 300.1 using a Dionex 500 ion chromatograph. Trihalomethanes (THMs) were analysed with Varian 3400 GC using "Purge and Trap" method.

Water characteristics

Table 1 reports the comparison of Fortore and Mosina pilot plant influent water characteristics.

Table 1. Fortore and Mosina water characteristics. Average.

Parameters	Fortore pre-treated water	Mosina pre-treated water
pH	7.5–7.9	7.06–7.48
Dissolved oxygen [mg/L]	9.0–10.4	6.68–9.94
COD [mgO_2/L]	1.6–3.9	4.32–6.90
TOC [mg/L]	1.0–4.0	3.26–7.98
Total coliforms [n°/100ml]	$1.5 * 10^3$	$1.2 * 10^3$

Granular activated carbons

Norit Row 0.8 Supra (vegetal), (Netherlands) was used in Mosina. In Fortore plant, Camel anthrafilter yv 115, vegetal and anthrafilter zm 90, mineral were used. GAC properties are reported in Table 2:

Table 2. GACs characteristics

		Camel yv 115	Camel zm 90	Norit 08
Granulometry	mm	0.8–1	1	0.8
Density	g / L	470–520	450–500	390
Humidity	%	< 5	< 5	<5
Hardness	%	97	90	97
Abrasion index	%	85	80	80
Iodine number	mg/g	1100	1000	1000
Blu Methylene	mg/g	160	230	150
Ash	%	< 4	< 4	<5

3. Results

Chlorites removal efficiency was examined in both, Mosina and Fortore pilot plants. In both cases the concentration of chlorites in GAC influent water was relatively constant, however in Fortore the amount of chlorite ions was significantly higher as a result of higher dosage of ClO_2 applied for the pre-disinfection in Fortore (1.1 mgClO_2/L) in comparison with Mosina (0.4 mgClO_2/L).

The removal of chlorite ions on GAC was performed until the breakthrough of the filters. Fig. 3a shows that in Fortore the breakthrough point, i.e. 0.2 mgClO_2^-/L was observed after the passing of 5000–5500 and 9000–10 000 bed volumes for mineral and vegetal GAC, while in Mosina up to 11 000 bed volumes of water passed through the Norit GAC filter without the breakthrough (Świetlik *et al*. 2002).

The study of chlorites removal on GAC filters conducted in Fortore pilot plant showed very high efficiency of the process (>95%) up to 4000 bed volumes (Fig. 3b).

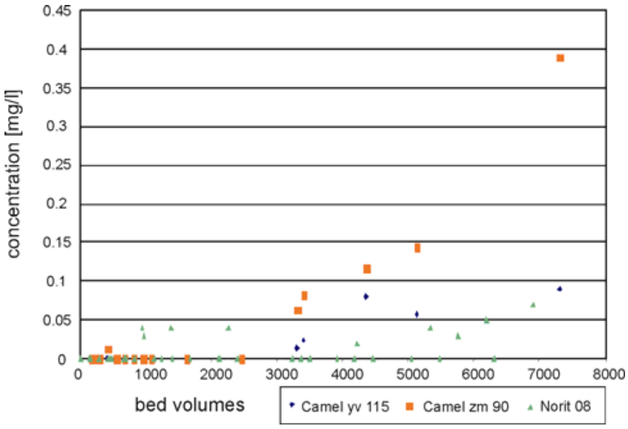

Fig. 3a. Comparison of chlorites concentration in GAC filter effluents

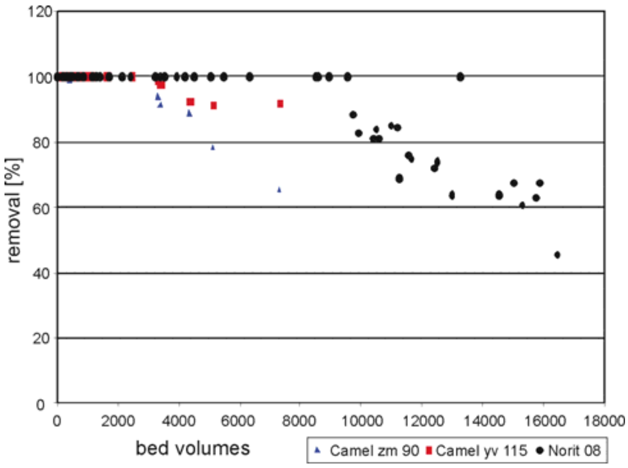

Fig. 3b. Percentage of chlorites removal after GAC filtration in Mosina and Fortore

In Mosina chlorites were effectively removed (~90%) up to 11 000 bed volumes (Świetlik *et al.* 2002). However, in Fortore in the first period of two months the removal of chlorites was in the range of 70 to 100% and the concentration of chlorites in effluent water does not exceed 0.1 mg/L. Higher efficiency of chlorites removal was observed for Camel vegetal GAC.

It must be emphasized, however, that GAC filters in Mosina were backwashed regularly. It means that GAC filters in Fortore pilot plant should require more regular backwashing to improve its efficiency of chlorites removal.

The concentration of dissolved NOM in both, Mosina and Fortore pilot plants raw waters was measured as well. The average concentration of TOC in Mosina was about 6 mg/L while in Fortore water TOC was in the range of 1–4 mg/L, with an average of 2.5 mg/L (Ranieri *et al.* 2007).

The studies of NOM adsorption on GAC were carried out in both, Mosina and Fortore pilot plants.

NOM removal by GAC in Mosina plant has been discussed in previous work (Świetlik 2002, 20003). In Fortore plant after sand filtration TOC was approx 1.3 mg/L for no pre-disinfected water and 1.1 mg/L for pre-disinfected water.

NOM removal expressed as TOC was quite low in both cases, particularly for ClO_2 predisinfected waters where TOC removal percentage was always lower than 30% and decreasing with time/filter bed volumes as shown in Fig. 4a. But after 8000 bed volumes the ClO_2 removal percentage become higher than in the other case.

As shown in Fig. 4b, after 10 000 bed volumes TOC concentrations still remain below 0.9 mg/L while in no pre-disinfected water TOC is more than 1.0 mg/L.

Preliminary characterization of Fortore water performed by HP-SEC indicated that natural organic matter present in Fortore raw water is mainly composed of molecules with low molecular sizes, < 500 Da.

These are typically small molecular weight components such as polysaccharides and proteins and are often indicative of biologically derived material (Leenheer 1981; van Leeuwen *et al.* 2002; Buchanan *et al.* 2005). Specifics of the technique and definitions have been described elsewhere (Chow *et al.* 2004).

ClO_2 pre-disinfection result in increasing of small molecular formation due to the intense reaction between NOM and ClO_2 (Dąbrowska *et al.* 2003; Raczyk-Stanisławiak *et al.* 2004). In fact chlorine dioxide reacts with Fortore's NOM continuously, until partial disappearance of NOM or ClO_2.

Low molecular sizes of NOM molecules make difficult the adsorption on GAC because the part of low molecular weight is less well retained by the GAC filter beds (Świetlik *et al*. 2002).

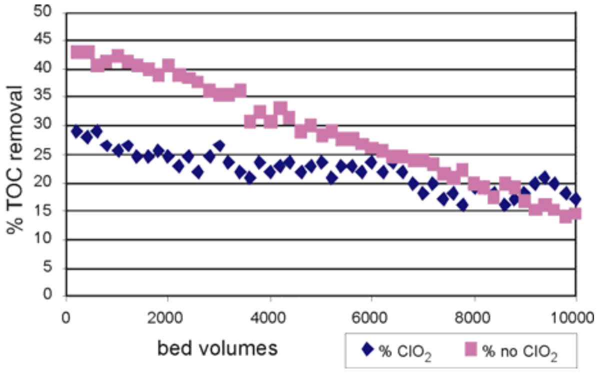

Fig. 4a. TOC removal in the GAC vegetal column *vs.* time in Fortore pilot plant

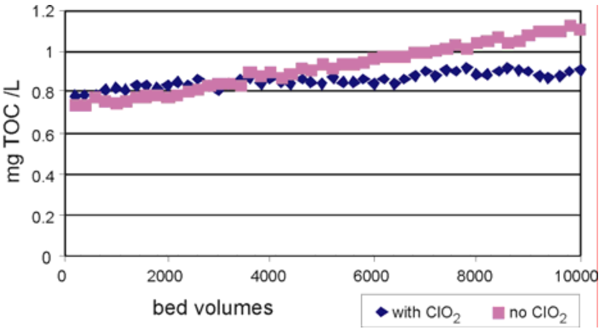

Fig. 4b. TOC concentrations in the GAC vegetal column *vs.* time in Fortore pilot plant

The low molecular weight of NOM Fortore raw water result in a very high reactivity of dissolved organic compounds in Fortore waters towards chlorine, and chlorine dioxide. This reaction between NOM and chlorine dioxide forms carboxilic acids while the presence of free chlorine results in significant amounts of THMs (Bellar *et al*. 1974; Rook 1974).

Therefore the pre-disinfection of Fortore raw water with chlorine is associated with serious risks of THMs formation.

Otherwise in temperate environments, such as those where Fortore plant operates, THM levels in drinking water are significantly affected by high temperatures that result in higher THMs concentrations (Singer *et al.* 1995; Arora *et al.* 1997; Chen and Weisel 1998; Rodriguez and Serodes 2001; Sadiq *et al.* 2002).

Fortore water pre-disinfected with chlorine dioxide and free chlorine contains also amounts of THMs, i.e. 46 μg/L as average of the sum.

The investigation on GAC filters THMs removal showed quite the same high efficiency: 70% as average, for vegetal GAC and approx. 65% for mineral GAC. Results are reported in Fig. 5.

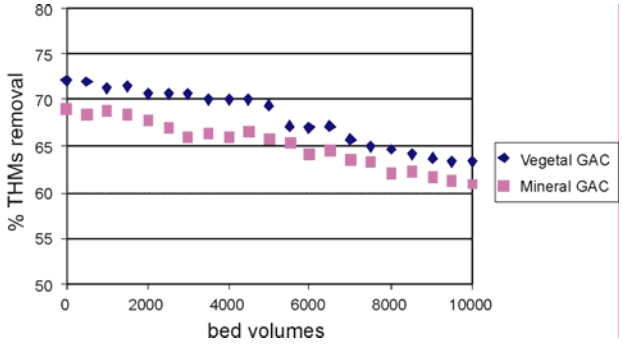

Fig. 5a. THMs (sum) removal as a function of bed volumes

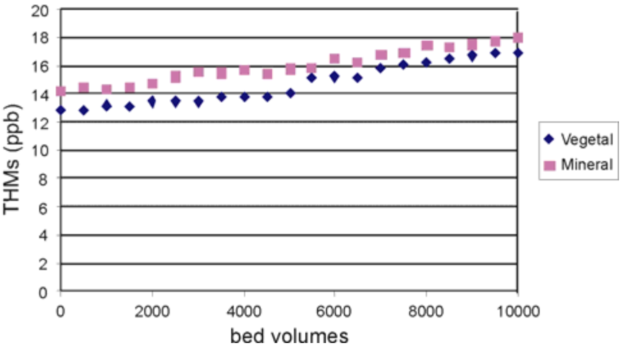

Fig. 5b. THMs (sum) concentrations as a function of bed volumes

Fig. 5b shows that in the GAC effluent THMs sum concentrations are constantly below 20 μg/L even after 10000 bed volumes respecting national directives on drinking water so that adsorption represents an essential step in the drinking treatment processes.

4. Conclusions

1. A quite high efficiency of chlorites removal, ranging from 60% to 95% up to 10 000 filter bed volumes, by GAC columns was observed in both, Mosina (Poland) and Fortore (Italy), drinking water pilot treatment plants. Vegetal GAC was more effective in chlorite ions removal after 5000 bed volumes. Slight differences in GAC performances should be explained also with different backwashing frequency.

2. A significant portion of the NOM in Fortore raw water is constituted by low molecular weight, < 500 Da; this result in an higher reactivity with chlorine dioxide and chlorine, so that carboxylic acids and THMs were found after $ClO_2 – Cl_2$ pre-disinfection.

3. NOM adsorption by GAC was quite low ranging from 19 to 43% as a function of operational time. After 10000 filter bed volumes GAC columns have shown a better behaviour in NOM removal for ClO_2 predisinfected water with a 20% higher removal efficiency than non predisinfected water.

4. A significant decrease, approx 70%, of THMs concentration in water after GAC filtration was observed either for vegetal and mineral carbon columns up to 10000 bed volumes.

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DBPs KONTROLĖ EUROPOS GERIAMOJO VANDENS ĮRENGINIUOSE IR VANDENS VALYMO EFEKTYVUMO TYRIMAI NAUDOJANT CHLORO DIOKSIDĄ

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Santrauka

Straipsnyje pateikiami eksperimentų, darytų atliekant DBPs kontrolę Fortore (Foggia, Pietų Italija) ir Mosina (Poznan, Lenkija) geriamojo vandens ruošimo įrenginiuose, rezultatai. Eksperimentiniai skirtingos rūšies GAC filtrai, skirti chlorido, natūralių organinių medžiagų (NOM) ir THMs šalinimo efektyvumui nustatyti, buvo įrengti abiejuose vandens ruošimo įrenginiuose. Abu eksperimentiniai vandens ruošimo įrenginiai veikė atlikus pirminį dezinfekavimą chloro dioksidu ir dezinfekavimo neatlikus. Fortore vandens ruošimo įrenginiuose laisvąjį chlorą pridedant į ClO_2 pirminės dezinfekcijos tirpalą, vertinta THMs susidarymas. Iš rezultatų buvo akivaizdu didelis chlorito sulaikymo GAC filtrais efektyvumas Fortore ir Mosina gyvenvietėse. Taip pat nustatytos preliminarios NOM, ištirpusių neapdorotame Fortore vandenyje, charakteristikos, taigi patvirtintas reaktyvumas su chloro dioksidu. Mažų molekulių (<500 Da) buvimas Fortore nedezinfekuotame vandenyje lėmė THMs ir karboksilinės rūgšties susidarymą dėl greitos reakcijos su Cl_2–ClO_2. Tyrimų duomenimis, THMs pašalinta nuo 60 iki 72 %, TOC – nuo 14,6 iki 43 %, taigi ši adsorbcija yra svarbus etapas kontroliuojant DBPs.

Reikšminiai žodžiai: chloro dioksidas, chloritai, granuliuotoji aktyvintoji anglis, NOM, THM.

ИССЛЕДОВАНИЕ КОНТРОЛЯ ПОБОЧНЫХ ПРОДУКТОВ ДЕЗИНФЕКЦИИ НА ЕВРОПЕЙСКИХ ОЧИСТНЫХ СООРУЖЕНИЯХ ПИТЬЕВОЙ ВОДЫ С ПРИМЕНЕНИЕМ ДИОКСИДА ХЛОРА

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Резюме

В статье представлены результаты экспериментов по осуществлению контроля побочных продуктов дезинфекции на очистных сооружениях питьевой воды в Форторе (Фоджия, Южная Италия) и Мосине (Познань, Польша). Экспериментальные фильтры GAC были установлены на обеих водоочистных установках с целью выявить эффективность разных фильтров GAC, предназначенных для очищения воды от хлорида и других вредных веществ. Обе экспериментальные водоочистные установки действовали с первичной дезинфекцией с применением диоксида хлора и без него. В Форторе, где в водоочистных установках в раствор ClO_2 для первичной дезинфекции добавляли свободный хлор, оценивалось образование тригалометана. Результаты показали высокую эффективность очищения от хлоридов фильтрами GAC в Форторе и Мосине. Также установлены предварительные характеристики естественных органических веществ, растворенных в необработанной воде в Форторе. Небольшое количество молекул (< 500 Da) в недезинфицированной воде в Форторе обусловило образование тригалометана и карбоксилановой кислоты в зависимости от скорости реакции с Cl_2–ClO_2. Фильтры GAC обеспечили 60–72-процентную очистку от тригалометана, а TOC – 14,6–43-процентную очистку. Таким образом, эта адсорбция является важным этапом контроля за побочными продуктами дезинфекции.

Ключевые слова: диоксид хлора, хлориды, гранулированный активированный уголь, тригалометан.

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