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Effect of Oxidation with Chlorine Dioxide on the Adsorption of Natural Organic Matter on Granular Activated Carbon

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Abstract

Chlorine dioxide is widely used as a pre-oxidant and disinfectant but it has the disadvantage of inducing the formation of the inorganic by-products chlorites and chlorates. It is therefore of interest to decrease the chlorine dioxide demand and oxidation, and/or removal of natural organic matter (NOM). The objective of this study was to estimate the efficiency of the adsorption of oxidised and unoxidised NOM on granular activated carbon (GAC) filters. For this purpose, three pairs of columns filled with three types of GAC were set. The study showed that the efficiency of adsorption increased after the pre-oxidation of NOM with $C1O_2$. GAC filters also efficiently removed the unwanted inorganic by-products.

Keywords: adsorption, chlorine dioxide, GAC, NOM, water treatment

Introduction

ClO_2 is mainly used as a final disinfectant but is also applied to control tastes and odors as well as to control biological growth at the early and intermediate stages of water treatment technology [1, 2, 3]. Chlorine dioxide works as an oxidating but not a chlorinating agent, and this is why it almost does not form trihalomethanes (THMs) during water treatment. The disadvantage of CIO2 application is the formation of inorganic by-products: chlorites and chlorates. Usually 1 mg of chlorine dioxide produces about 0.7 mg chlorite and a different (usually lower) amount of chlorate. The Maximum Contaminant Levels (MCLs) of the by-products vary from country to country, but never exceed 1.0 mg ClO_2/L and 0.24 mg ClO_3/L [4]. There are no regulations controlling the level of neither $C1O_2$ nor its by-products in Poland. It seems to be at least controversial, as ClO_2 is commonly used in water treatment plants.

It is therefore reasonable to look for methods that can decrease the necessary amount of chlorine dioxide used for disinfection, i.e. to decrease ClO_2 demand. The demand is mainly caused by iron (Fe(II)), manganese (Mn(II)), nitrites and natural organic matter (NOM). The latter seems to be the most important as the metals can be efficiently removed by aeration and sand filtration. Thus, NOM-caused demand should be decreased. Oxidation of NOM, removal of NOM or both can accomplish that task. The often-used ozonation of NOM is still considered to be an expensive process. Thus, from an economic point of view it is reasonable to verify the application of ClO_2 as the oxidant followed by GAC filtration for the removal of oxidised NOM and inorganic by-products. It has been reported that GAC filtration efficiently removes chlorites [5, 6].

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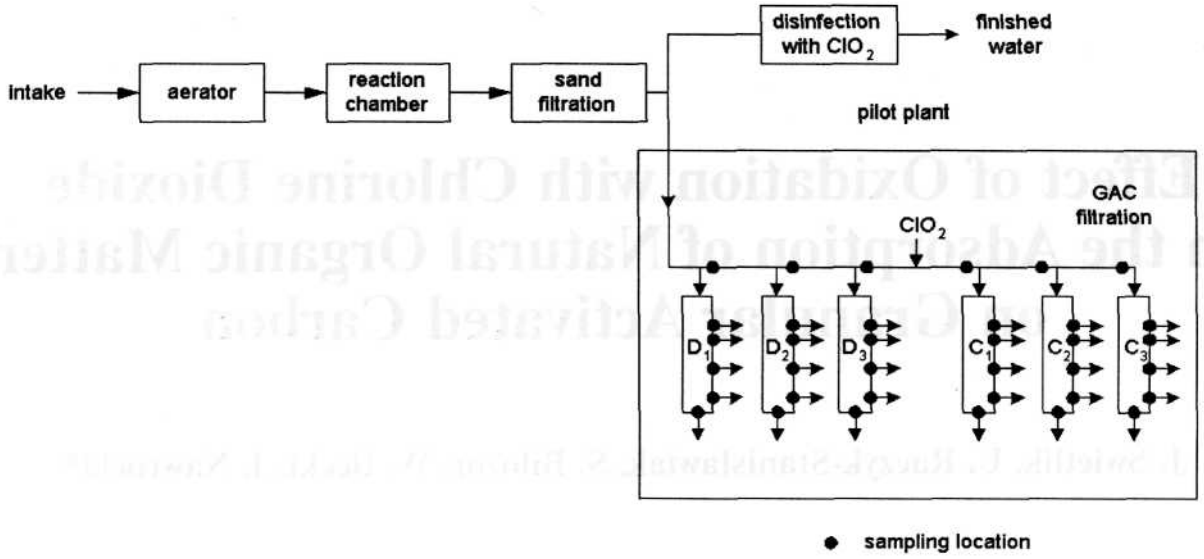

Fig. 1. Mosina Water Treatment Plant and Pilot Plant.

The literature lacks data about the effect of oxidation with ClO_2 on the adsorption of NOM on granular activated carbon There are also no reports about the influence of preoxidation with small doses of ClO_2 on water organic micropolutants' molecular weight distribution.

The purpose of the study presented in this paper was to examine the efficiency of NOM adsorption on GAC subsequent to ClO_2 oxidation. NOM adsorption effectiveness was described by:

- decrease of total organic carbon (TOC) in the water during the filtration on GAC;
- decrease of ClO_2 demand of the water in the GAC filters' outlet;
- determination of the amount of organic substances adsorbed on different types of GAC;
- changes in the molecular weight distribution of NOM presented in the water before and after GAC filtration.

Experimental Procedures

Water Treatment Processes

The pilot plant (Fig. 1) is located at the Water Treatment Plant in Mosina (Poznari Water Treatment and Sewage Co.). The influent of the pilot plant is the underground water from the Mosina Water Intake (MWI). The intake contains two barriers of wells located along the river Warta. The water supplied by the lower barrier is influenced by the infiltration of water from the river, however, the composition of water from both barriers does not differ very much. The raw water is aerated and filtered through the sand filters to remove excess iron and manganese.

The experiments were carried out in two parallel sets of columns (C and D, 6.2 cm i.d. and 1 m height) filled with virgin GACs: Norit Row 0.8 Supra (Germany)(Cl and Dl), Chemviron F300 (C2 and D2) and Chemviron F400 (Germany) (C3 and D3). Table 1 shows the main characteristics of the GACs used in this study. Each column was fitted with special sampling ports for the collection of water samples at five bed depths (20, 30, 50, 75 and 100 cm, respectively). The flow rate was 5 m/h. Preoxidation of water with 0.4 mg ClO_2/L, which is an equivalent to about 50% of ClO_2 demand, was applied for three filters (C1, C2, C3).

Table 1. Properties of GAC used in experiments.

	Norit Row 0.8 Supra	Chemviron F300	Chemviron F400
Surface area of pores > 2nm [m^2/g]	123.2	105.6	123.7
Average pore volume [cm^3/g]	0.25	0.20	0.23
Average pore diameter of pores > 2 [nm]	5.7	5.1	5.2
Total surface area [m^2/g]	840.8	867.1	916.5

TOC Measurement

Total organic carbon (TOC) was analysed by LAB-TOC system (Pollution and Process Monitoring Ltd., England) total organic carbon analyser using the method of sodium peroxydisulfate/orthophosphoric acid wet oxidation and UV radiation. Peroxydisulfate combined with UV light converts all the organic carbon present in the sample to carbon dioxide. The amount of carbon dioxide was measured with an IR detector and relayed to the computer.

Size Exclusion Chromatography (SEC)

The chromatographic characterisation and molecular weight distribution of NOM was determined by high performance size exclusion chromatography (SEC) using UV-detection at 254 nm (AD 25 detector, Dionex, USA) on a DIONEX DX-500 Chromatography System with TosoHaas TSK gel G 3000 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 without the addition of buffer. All analyses were performed at a temperature of 30°C.

Calibration was carried out using peak maximum calibrations with sodium polystyrene sulphonate standards (30900 D, 13400 D, 4850 D, 1120 D, 172 D) (PSS Polymer Standards, Germany) [7]. Molecular weight, which is related to the size of solute molecules, was plotted against retention time. The ordinate scale was logarithmic.

Membrane Filtration

The enrichment of water samples (with molecules of M < 1000 Da and with molecules of M > 1000 Da) was performed by means of membrane techniques. The membrane filtration experiments were carried out using the Membrane System 3XS28 from OBR Pleszew (Poland). The system consisted of two membrane modules (UF, NF), 170 L stainless steel tank, covered by a stainless steel lid, and the steel frame containing the other components of the system. The circulating pump (Grundfos) had a maximum operating pressure of 1 MPa. The properties of the membranes are:

Parameter	UF membrane	NF membrane
Cut-off	50 kD	1 kDa
Membrane material	$Al_2O_3/TiO_2/ZrO_2$	$Al_2O_3/TiO_2/ZrO_2$
Number of canals	23	23
Total surface area	0.35 m^2	1.05 m^2
Membrane diameter	25 mm	25 mm
Length	1178 cm	1178 cm
Manufacturer	Tami Industries, France	

Chlorine Dioxide Demand Measurement

Chlorine dioxide demand was determined by photometric method with N,N-diethyl-l,4-phenylenediammoniumsulphate (DPD). Absorbance was measured with a HACH DR/4000 UV/VIS spectrophotometer at 515 nm, in 1-inch glass cell [8].

The by-products chlorite and chlorate were determined by ion chromatography with a DIONEX DX-500 system with IonPac AS-9-HC analytical column (4x250 mm) and IonPac AG9-HC guard column (4x50 mm), connected with a conductivity detector CD-20 (Dionex, USA).

Results and Discussion

The water at the Mosina Water Intake (MWI) usually contains 3.8-6.5 mg L^{-1} of total organic carbon. TOC level may vary considerably in a relatively short period of time. The chlorine demand of MWI water oscillates between 0.50 and 0.82 mg/L.

NOM size distribution of water from MWI, untreated and ClO_2 treated was characterised by SEC. The results reveal the TOC to be composed of molecules with nominal molecular weights placed in the range of 1900-360 Da. Figure 2 presents how the molecular weight distribution of NOM is influenced by ClO_2 treatment.

Fig. 2. Molecular size distribution of NOM from Mosina Water Intake by SEC.

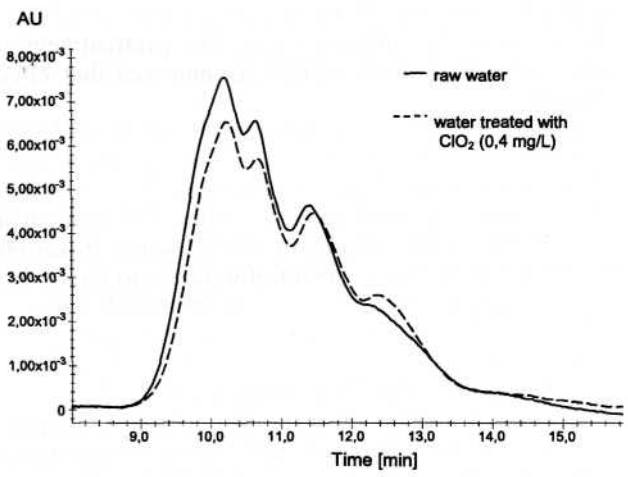

Figure 2 shows that ClO_2 does not substantially change the UV-active fraction of NOM. However, small changes in the molecular size distribution of NOM were detected. The absorbance of higher molecular weight fractions (1900-1000 Da) decreased while the absorbance of the fraction of molecular weight below 500 Da slightly increased as a result of oxidation. Figure 2 also proves that fractions of higher molecular weight are more susceptible to reaction with ClO_2 than compounds of lower molecular weight. This confirms that the high ClO_2 demand is caused mainly by the high molecular part of the NOM.

The separation of NOM into the fractions enriched with molecules of M < 1000 Da and with molecules of M > 1000 Da by membrane techniques was performed. The ClO_2 demands for the separated fractions of NOM calculated per 1 mg C_{org} are shown in Fig. 3. This confirms again that ClO_2 demand is caused mainly by the NOM molecules with nominal molecular weights above 1000 Da.

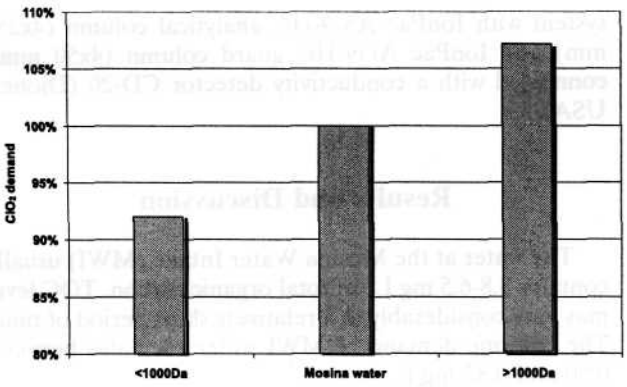

Fig. 3. The dependence of ClO_2 demand on molecular weight of NOM.

During the pilot study one of the main purposes was to develop methods for effective NOM removal. Two sets of GAC filters were applied. Filtration through activated carbon bed decreased ClO_2 demand about 0.15-0.3 mg/L compared to the influent water. The pretreatment of water with small doses of ClO_2/L improved that effect (Fig. 4).

During the filtration process TOC content and ClO_2 demand of treated and untreated water samples taken from various levels of the filter beds were measured. Figures 5a and 5b present changes in the TOC content in the effluents vs. the volume of filtered water. It was observed that ClO_2 pretreatment of water considerably improved the adsorption efficiency of the NOM. After filtration of 1600 bed volumes of water, the TOC of untreated water was higher than 2 mg C_{org}/L while for treated water it still did not exceed 1 mg C_{org}/L.

Figures 6a and 6b show the SEC chromatograms of ClO_2 treated and untreated water. After the passing of 1670 bed volumes of water through the filters, the molecular size distribution of organic matter eluting from the filters exhibited marked differences. The filtered water previously treated with ClO_2 contained an exclusively low molecular size fraction of NOM with nominal molecular weight not exceeding 500 Da. The untreated water contained additional fractions of a higher molecular weight.

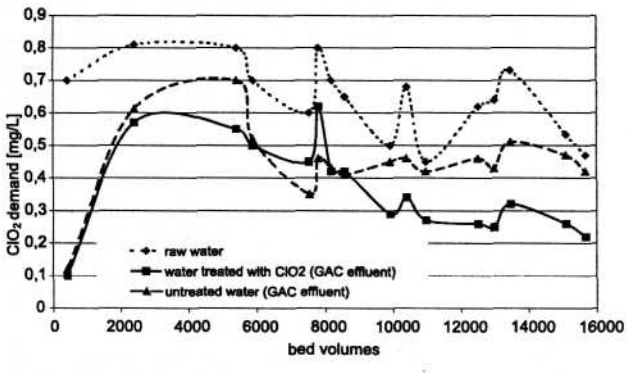

Fig. 4. The ClO_2 demand of GAC effluents.

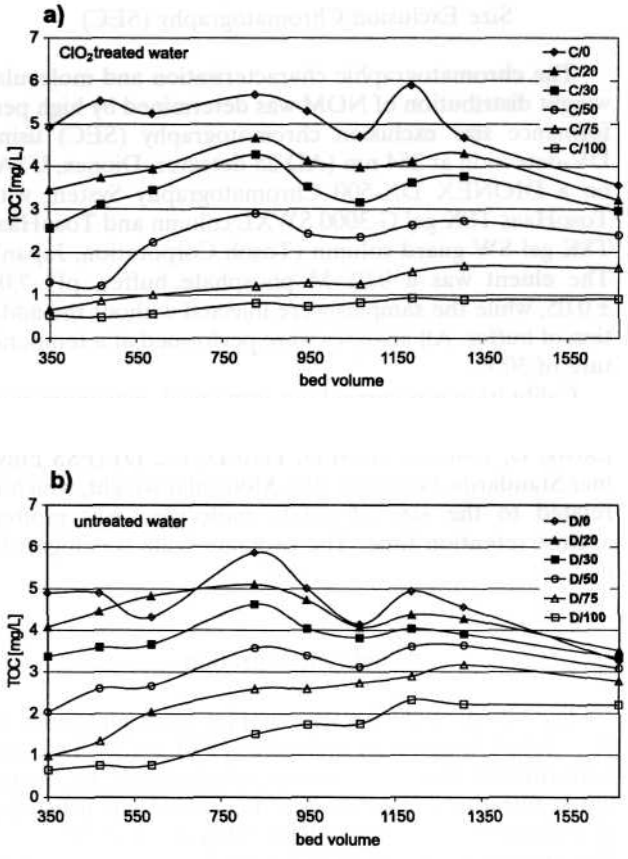

Fig. 5. TOC changes on particular levels of GAC filters: a) ClO_2 treated water, b) untreated water.

This means the high molecular fraction of NOM from water treated with ClO_2 appears to be adsorbed on the GAC filter to the higher level in comparison with that from untreated water. This phenomenon is technically useful, as high molecular weight fraction of NOM is the leading cause of high ClO_2 demand.

The examination of the NOM adsorption efficiency on three types of commercially available GAC was performed. The filters were supplied by water treated with 0.4 mg ClO2/L and untreated water. It was confirmed that ClO2 pretreatment of water could considerably improve the adsorption capacity of the GAC filters. Table 2 presents the total adsorption efficiency for all examined circumstances. For untreated water considerable differences in the adsorption ability on particular carbon filter beds were found, while for ClO_2 treated water the differences were insignificant. What is more, the filtration process was generally more potent for ClO_2 pretreated water. Chemviron F-400 however appeared to give the most satisfactory effects for both treated and untreated water.

It has been frequently reported that GAC filters retain chlorites very effectively [6]. In the reported experiments the removal efficiency of inorganic ClO_2 by-products, i.e. chlorites and chlorates, with GAC filtration was examined. The substantial reduction of the amount of chlorites over a large amount of water passing the GAC filters was observed (Fig. 7).

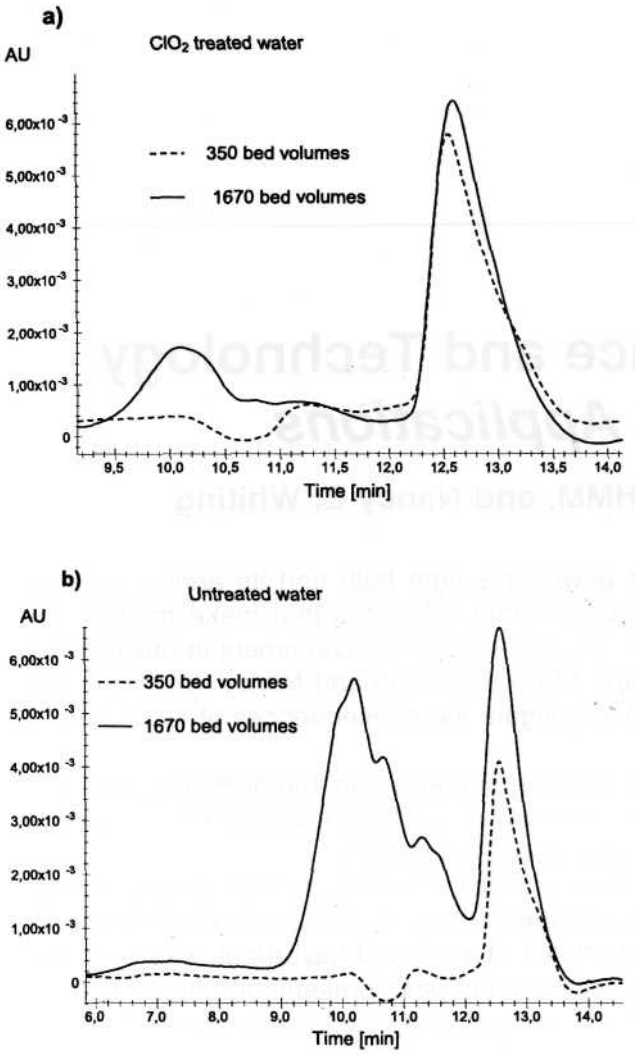

Fig. 6. Molecular size distribution of organic matter eluting from GAC: a) ClO_2 treated water, b) untreated water.

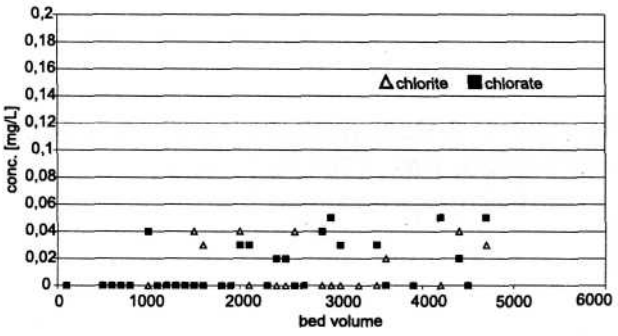

Fig. 7. Chlorites and chlorates in GAC effluent of ClO_2 treated water.

Moreover, a small amount of chlorates eluting from the GAC filters was detected, however their concentration never exceeded 0.05 mg/L. Thus, we can undoubtedly confirm the very high capacity of GAC filters in relation to chlorites.

Table 2. Total adsorption efficiency of NOM on commercially available GAC [g of adsorbed TOC/1 g of GAC] (3300 bed volumes).

	Norit	F-300	F-400
Water treated with 0.4 mg ClO_2/L	0.0258 g/g	0.0209 g/g	0.0242 g/g
Untreated water	0.0173 g/g	0.0155 g/g	0.0221 g/g

Conclusions

This paper shows that the pretreatment of water with small doses of ClO_2 followed by GAC filtration considerably improves total adsorption efficiency of NOM on granular activated carbon. ClO2 demand is correlated with TOC value. In consequence, the decrease of TOC level leads to lower ClO_2 demand of treated water. The GAC filtration also effectively removes chlorites.

Acknowledgement

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