Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20244

64 (2017) 165–172
February

Removal of chlorite from drinking water: laboratory and pilot-scale studies to predict activated carbon performance at full scale

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Received 27 July 2016; Accepted 29 September 2016

ABSTRACT

Chlorite is a by-product that can be produced in the disinfection process of a drinking water treatment plant (DWTP) using chlorine dioxide. The aim of this work was to evaluate the influence of the adsorption process with activated carbon on chlorite removal and to demonstrate how laboratory-scale and pilot-scale tests can be useful to predict granular activated carbon (GAC) performance on chlorite removal at full scale in a DWTP. A first series of tests were carried out at laboratory scale using small carbon columns. A second series of tests were performed at semi-full scale using a pilot plant at the DWTP of Vescovana (Padova, Italy). The laboratory-scale tests show that carbon pre-loading significantly reduces the ClO_2^- removal yield, by about 30%–40%. Both laboratory-scale tests and small column tests show that in virgin conditions the mineral carbon shows a higher ClO_2^- removal efficiency than the vegetal one, while in pre-loaded conditions an opposite behavior is observed. The results of the pilot plant test show that GAC ensures a good ClO_2^- removal yield, close to 55%. The results show that small column tests at laboratory scale are extremely useful to predict pilot column performance and, therefore, full-scale DWTP performance.

Keywords: Activated carbon; Chlorite; Drinking water treatment plant; Laboratory scale; Pilot plant

1. Introduction

Water disinfection is usually the last process in a drinking water treatment plant (DWTP) to prevent microbial contamination in the distribution network. However, this process requires the use of chemical disinfectants that can produce unwanted disinfection by-products (DBPs) with potential health concerns. In particular, if chlorine is used in final disinfection it can react with natural organic matter (NOM) to produce halogenated DBPs, especially trihalomethanes (THMs) and haloacetic acids (HAAs) [1]. Since total THMs increase with the chlorine dose, it is important to evaluate the use of alternative disinfectants [2]. Chloramines can form THMs, trihalogenated HAAs, dihalogenated HAAs, *N*-nitrosodimethylamine, and total organic halogen (TOX), although generally lower than that from chlorination [3–5]. Concerning ozone, one of its main DBPs is bromate that increases with ozone dose and bromide concentration; ozone is not usually used in final disinfection because it does not provide a residual protection in the distribution network [2]. Concerning ultraviolet (UV) disinfection, it can produce concentrations of nitrite directly dependent on the UV dose applied and the nitrate concentration in water and aldehydes can be formed as a result of the UV irradiation of solutions of humic acid [6]. Moreover, UV disinfection does not provide residual protection in the water distribution system [7].

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For these reasons, there is an increasing interest about the use of chlorine dioxide (ClO_2) as alternative disinfectant in DWTPs. Disinfection with ClO_2 is commonly applied in DWTPs as it is more effective than chlorine or chloramines as disinfectant against micro-organisms, it controls taste and odor better than chlorine in some cases, and it forms less THMs, HAAs, and TOX than free chlorine [7,8]. Moreover, it ensures a residual concentration of free chlorine at the point of delivery at or above 0.2 mg L^{-1} [9–13]. However, ClO_2 can react with NOM to produce unwanted DBPs, such as chlorite (ClO_2^-) and chlorate (ClO_3^-) [13]. Since the exposure to these compounds can determine oxidative damage to red blood human cells, the World Health Organization fixed a regulation limit of 5 mg L^{-1} for chlorine dosage in disinfection and 700 μg L^{-1} for both ClO_2^- and ClO_3^- in drinking water [13–16]. In order to minimize ClO_2^- and ClO_3^- formation in final disinfection, ClO_2 demand in final disinfection can be reduced [17]. Different treatment processes can be employed for ClO_2^- removal, such as reduction with ferrous ions, adsorption with activated carbon, oxidation with ozone, and reduction with sulfur compounds [18–21]. In particular, granular activated carbon (GAC) can remove ClO_2^- because of adsorption and chemical reduction [20,21]. Under typical drinking water conditions (<1–2 mg L^{-1} ClO_2^-) a removal of 130 mg ClO_2^- per gram of GAC can be obtained with a GAC lifetime of about 8–12 months, an empty bed contact time (EBCT) of 10–15 min and a maximum ClO_2^- concentration in the effluent of 0.2 mg L^{-1} [22]. Moreover, the GAC performance in terms of ClO_2^- removal significantly varies if a virgin or a thermally regenerated GAC is used instead of an exhausted GAC. Some researchers found that thermally regenerated GAC demonstrates good removal for both organic matter (70%–80%) and ClO_2^- (100%). With exhausted GAC, organic matter removal can be reduced from 40%–50% (without ClO_2^-) to 5%–7% (when water is spiked with ClO_2^-) while ClO_2^- removal remains significant, with yield of about 50% [20]. Other important factors that influence the ClO_2^- removal are the effect of GAC pre-loading and the EBCT [23]. Some authors observed that GAC pre-loaded with NOM has a low ClO_2^- removal efficiency (15%–20%) and an increase in EBCT from 2 to 10 min increases the removal efficiency from 30% to 80% [21].

Several tests are available at the laboratory scale or at the pilot scale in order to predict the GAC performance at the full scale in terms of ClO_2^- removal. A test aimed at comparing the adsorption capacity of different activated carbons is the Freundlich isotherm determination at the laboratory scale in batch conditions. Some researchers determined the Freundlich isotherms related to the ClO_2^- removal and found that mineral meso-porous activated carbons allow a higher ClO_2^- removal than the vegetal micro-porous GACs; in particular, using the mineral carbons, a maximum ClO_2^- removal of 99% was obtained with demineralized water, 80% with groundwater, and 70% with surface water [19]. Moreover, rapid small-scale column tests (RSSCTs), pilot-scale tests, and mathematical models can be studied to predict GAC performance at the full scale. Pilot studies can predict full-scale GAC performance very accurately; however, they require very long time to obtain results, they are expensive and must be conducted onsite [24]. Some authors tested pilot columns containing virgin and pre-loaded GACs; they reported a ClO_2^- removal of 93%–96% using the virgin GACs and of 13%–21% using the pre-loaded GAC [21]. RSSCTs can also predict the GAC full-scale performance accurately, without isotherm studies; moreover, they require a small volume of water and they can be conducted in a fraction of time required to conduct pilot studies. Consequently, replacing a pilot study with an RSSCT significantly reduces the time and cost of a full-scale design. However, the results of RSSCT are site specific and only valid for the raw water tested [24]. No specific data are available in the literature concerning the use of RSSCT to evaluate the ClO_2^- removal. However, some authors compared RSSCTs to pilot columns for the removal of background dissolved organic carbon in five surface waters and one groundwater and reported that the RSSCT data agrees well with the pilot column data [25]. Mathematical models, once calibrated, can be used to predict the impact of EBCT and changes in the influent concentration, but they cannot predict the total organic carbon breakthrough and must be used in conjunction with pilot or RSSCT data. However, they can predict the breakthrough of synthetic organic compounds with 20%–50% error, but only after a calibration with pilot or RSSCT data [24].

Predicting the GAC performance at the full scale with laboratory- and pilot-scale tests allows to evaluate the implementation of a GAC treatment in a DWTP or to optimize the performance of an existing GAC stage.

This study presents the results of laboratory- and pilot-scale column tests using GAC to reduce the ClO_2^- concentration in drinking water. Small and pilot GAC columns were tested, comparing a mineral and a vegetal GAC, in order to evaluate the GAC performance on ClO_2^- removal in virgin and pre-loaded conditions. Therefore, this study has the objective to evaluate how these tests can be useful to predict the GAC full-scale performance in a DWTP. The results may be of interest for many water utilities that employ activated carbon in the DWTP treatment chain or are interested in upgrading the DWTP adding a GAC adsorption stage.

2. Methods

2.1. DWTP of Vescovana (Padova, Italy)

The DWTP of Vescovana (Padova, Italy) treats an average water flow of 24 ML d^{-1}. The plant treats surface water, from Adige river, with the following parameters to be lowered/removed: turbidity, iron, aluminum, total coliform, and *Escherichia Coli*.

The plant is composed of the following processes: pre-oxidation with ClO_2 and, occasionally, with sodium hypochlorite (NaClO); coagulation in tank with ferric chloride ($FeCl_3$), flocculation and sedimentation; granular filtration in mixed GAC-sand filters; GAC adsorption; and final disinfection with ClO_2.

2.2. Experimental design and methods

In order to evaluate ClO_2^- removal with GAC, two types of experimental test were performed (Fig. 1):

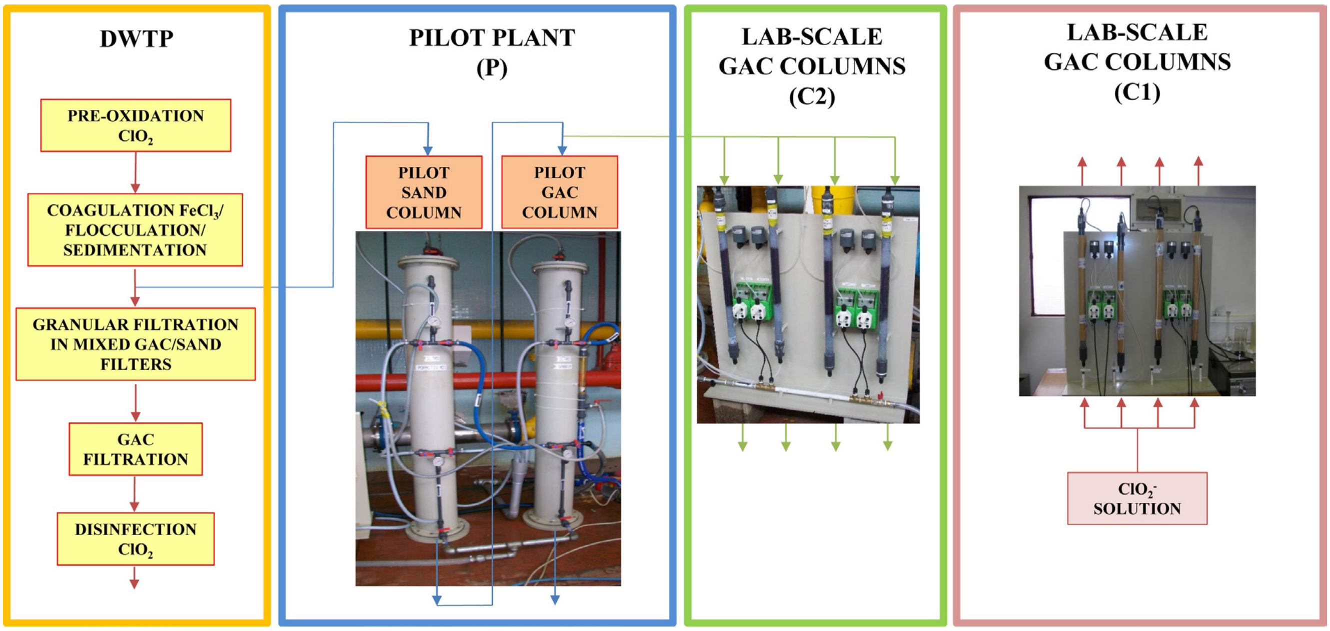

Fig. 1. Flow chart of the experimental tests.

- Adsorption with activated carbon with small continuous flow column tests at laboratory scale (C).
- Adsorption with activated carbon with continuous flow pilot plant at the DWTP at semi-full scale (P).

These tests were conducted by applying the operating conditions reported in Table 1.

Two activated carbons with different physicochemical characteristics were tested: a mineral GAC (Poractiv M21, Hydro-line) and a vegetal GAC (Poractiv C24, Hydro-line) (Table 2). In some cases (Table 1), carbons were also tested in pre-loaded conditions, in order to simulate the saturation of the various GAC pore fractions, thus to investigate GAC performance on chlorite removal in exhausted conditions. The GAC pre-loading was carried out by treating the virgin carbon (50 g) with a solution containing demineralized water (800 mL), methylene blue (13 and 14.5 g, respectively, for M21 and C24), iodine (48.5 and 60 g, respectively, for M21 and C24), and phenol (36 and 25 g, respectively, for M21 and C24). The chemicals employed for this goal were chosen on the basis of their molecular diameter. Indeed, methylene blue (molecular diameter of 1.5 nm) was used to pre-load GAC meso-pores, iodine (molecular diameter of 1.0 nm) and phenol (molecular diameter of 0.7–0.8 nm) were used to saturate GAC micro-pores. The pore dimensions were considered according to the International Union of Pure and Applied Chemistry. The virgin GAC was continuously mixed with this solution for 20 days to simultaneously homogenize all the compounds with carbon. The pre-loading achievement was evaluated by analyzing the methylene blue adsorption, the iodine number, and the phenol number for each carbon. In section 3, the pre-loading achievement is not shown, since it was not the objective of this study. After the saturation period, pre-loaded carbons were washed with distilled water to avoid release of excess compounds not adsorbed by GAC that could interfere during the subsequent water analysis. Then, the pre-loaded carbons were used in the column tests (Table 1).

2.3. Column tests at laboratory scale (C)

Two different column tests were carried out at laboratory scale in order to evaluate the GAC adsorption capacity in terms of ClO_2^- removal.

In the first column test (C1), four small columns (diameter = 3 cm and height = 62 cm), respectively, containing the mineral and the vegetal carbon (30–40 g), each in virgin and pre-loaded conditions, were tested. The columns, installed in parallel onto vertical panels, were connected to peristaltic pumps, which allowed a continuous upflow at a constant rate. Each column operated with a 5 min EBCT, a 1 L h^{-1} flow, and a 1.4 m h^{-1} hydraulic load (Table 1). The columns were fed with a ClO_2^- solution, prepared by adding $NaClO_2$ solution (31%) to demineralized water, with an initial ClO_2^- concentration of 1 mg L^{-1}. The virgin carbon and the pre-loaded carbon columns worked for a period of about 180 and 80 days, respectively. During the operating period, the residual ClO_2^- was analyzed on samples collected approximately once a day at the outlet of the columns.

In the second column test (C2), four small columns (diameter = 3 cm and height = 64 cm) were tested in different operating conditions (Table 1). Two columns were filled with the mineral carbon, one with the vegetal carbon, and one with the mineral pre-loaded carbon (80 g). The columns, installed in parallel onto vertical panels, were connected to peristaltic pumps, which allowed a continuous downflow at a constant rate. Water coming from the outlet of the sand column of the pilot plant (P) was used to feed the columns. During the operating period, ClO_2^- was analyzed on samples collected once a week at the outlet of the columns.

All the columns, both during C1 and C2 test, were never backwashed.

Table 1
Operating conditions of the experimental tests

Test		Feed	GAC	Operating conditions	Column dimensions and stratigraphy
Column tests (C)	C1	ClO_2^- solution	min, veg, min_P, veg_P	$Q = 1\ L\ h^{-1}$, EBCT = 5 min	• Dimensions: $d = 3$ cm, $h = 62$ cm • Stratigraphy (bottom upward): 1 cm cotton 12 cm glass spheres $d = 6$ mm 12 cm glass spheres $d = 3$ mm 12 cm GAC 12 cm glass spheres $d = 3$ mm 12 cm glass spheres $d = 6$ mm
	C2	Water out pilot sand column	min	• $Q = 1\ L\ h^{-1}$, EBCT = 10 min • $Q = 0.5\ L\ h^{-1}$, EBCT = 20 min	• Dimensions: $d = 3$ cm, $h = 64$ cm • Stratigraphy (bottom upward): 1 cm cotton 10 cm glass spheres $d = 6$ mm 10 cm glass spheres $d = 3$ mm
			veg	$Q = 1\ L\ h^{-1}$, EBCT = 10 min	24 cm GAC 10 cm glass spheres $d = 3$ mm
			min_P	$Q = 1\ L\ h^{-1}$, EBCT = 10 min	10 cm glass spheres $d = 6$ mm
Pilot plant (P)	Sand column	Water out coag/flocc/sed at the DWTP	–	$Q = 500\ L\ h^{-1}$, EBCT = 5 min	• Dimensions: $d = 25$ cm, $h = 2$ m • Stratigraphy (bottom upward): 20 cm gravel $d = 3–5$ mm 70 cm sand $d = 0.6–2.8$ mm 30 cm anthracite
	GAC column	Water out pilot sand column	min	$Q = 500\ L\ h^{-1}$, EBCT = 5 min	• Dimensions: $d = 25$ cm, $h = 2$ m • Stratigraphy (bottom upward): 20 cm gravel $d = 3–5$ mm 100 cm GAC

Note: min – mineral; veg – vegetal; min_P – mineral pre-loaded; veg_P – vegetal pre-loaded; coag/flocc/sed – coagulation/flocculation/sedimentation; d – diameter; h – height.

Table 2
Physicochemical characteristics of the activated carbons employed in the experimental tests

Parameter	Poractiv M21 (Hydro-line)	Poractiv C24 (Hydro-line)
Origin	Mineral	Vegetal
Porosity	Macro- and micro-porous	Micro-porous
Surface area Brunauer–Emmett–Teller, $m^2\ g^{-1}$	1,038	1,207
Iodine number, $mg\ g^{-1}$	970	1,204
Uniformity coefficient	1.61	1.64
Density, loose packed, $kg\ m^{-3}$	428	456
Density, dense packed, $kg\ m^{-3}$	463	491
Effective size, mm	0.75	0.76
Micro-pores volume, $mm^3\ g^{-1}$	197	461
Meso-pores volume, $mm^3\ g^{-1}$	123	42
Macro-pores volume, $mm^3\ g^{-1}$	233	58

2.4. Pilot plant at semi-full scale (P)

After the column tests, a pilot plant at semi-full scale was tested in order to evaluate the carbon adsorption capacity in terms of ClO_2^- removal in the DWTP. A pilot sand column (diameter = 25 cm and height = 2 m) followed by a pilot GAC column (diameter = 25 cm and height = 2 m) was installed after the coagulation, flocculation, and sedimentation process of the DWTP. The GAC column was filled with the mineral carbon, since it resulted the best carbon in terms of adsorption capacity from previous column tests at laboratory scale (C1 and C2). Both columns, made in polypropylene with 1/2″ polyvinyl chloride valves and 1/2″ manual vent, operated with a 5 min EBCT at a 500 $L\ h^{-1}$ flow (the flow was monitored by a flowmeter installed at the inlet of the pilot sand column) with a continuous downflow at a constant rate (Table 1). The backwash was made on both sand column and GAC column, by a single upflow backwash phase with water, for 1 h a day at a 3 bar pressure. The ClO_2^- concentration was analyzed on samples collected once a week at the inlet and outlet of the pilot sand column, and at the outlet of the pilot GAC column.

2.5. Analytical methods

The methylene blue adsorption, the iodine number, and the phenol adsorption were analyzed with a spectrophotometer (PerkinElmer Lambda 25) [26–28]. The ClO_2^- concentration was analyzed with Ion Chromatograph 761 Compact IC Metrohm [29].

3. Results and discussion

3.1. Column tests at laboratory scale (C)

In the first column test (C1), residual ClO_2^- was determined on samples collected at the outlet of the four GAC columns, each operating with a 5 min EBCT (Fig. 2).

Comparing the virgin carbons, the results show that the mineral GAC guarantees the complete ClO_2^- removal for about 3 months, while the vegetal GAC for about 1 month. Moreover, after 6 months the ClO_2^- concentration at the outlet of the mineral GAC column is half the one at the outlet of the vegetal one. Therefore, in virgin conditions the mineral GAC is more efficient than the vegetal. Further, with both the mineral and the vegetal GAC after 6 months the ClO_2^- concentration is significantly below the regulation limit of 700 μg L^{-1}.

Comparing the pre-loaded carbons, during the first month the mineral GAC shows a higher efficiency than the vegetal one; however, after this period the vegetal GAC shows a higher efficiency, reaching a removal yield twice than the mineral GAC after 80 days of operation. Therefore, in pre-loaded conditions the vegetal GAC is more efficient than the mineral, as opposed to the results obtained in virgin conditions.

Comparing virgin and pre-loaded carbons, the ClO_2^- trends at the outlet of the vegetal GACs are similar, while a significant difference is observed between the mineral GACs. In fact, since the vegetal carbon is micro-porous, ClO_2^- is less adsorbed both in virgin and pre-loaded conditions, with a negligible difference.

In the second column test (C2) (Fig. 3), the virgin mineral GAC operating with a 10 min EBCT guarantees a complete ClO_2^- removal for about 5 months, and then ClO_2^- is always below 200 μg L^{-1} till the end of the monitoring period. At the outlet of the virgin mineral GAC operating with a 20 min EBCT, a complete ClO_2^- removal is registered during all the monitoring period. These results show that a lower EBCT implies the breakthrough achievement in a shorter period. This suggest that with a higher water flow, thus with a lower EBCT, the GAC operates with a higher ClO_2^- load and, therefore, it rapidly achieves the breakthrough. Moreover, it is important to highlight that ClO_2^- removal by GAC is the product of two steps: ClO_2^- adsorption on GAC sites and its reduction to chloride, the primary final reaction product. Therefore, the ClO_2^- removal observed with a low EBCT is mainly due to the reduction of ClO_2^- to chloride, while the adsorption of ClO_2^- on the GAC active sites is a slower process that increases only at a higher EBCT [20].

Unlike the results of the C1 column tests (Fig. 2), in the C2 column test at the same flow and EBCT (Q = 1 L h^{-1}, EBCT = 10 min) in virgin conditions the vegetal GAC shows a greater ClO_2^- removal efficiency than the mineral GAC; in fact, considering the vegetal GAC column, a complete ClO_2^- removal is registered during all the monitoring period.

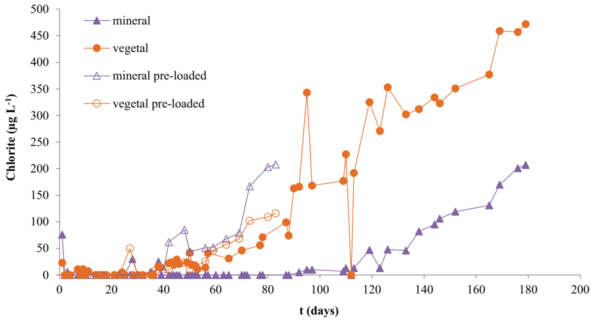

Fig. 2. Residual ClO_2^- concentration in samples collected at the outlet of the GAC columns operating with a 5 min EBCT, in the first column test (C1).

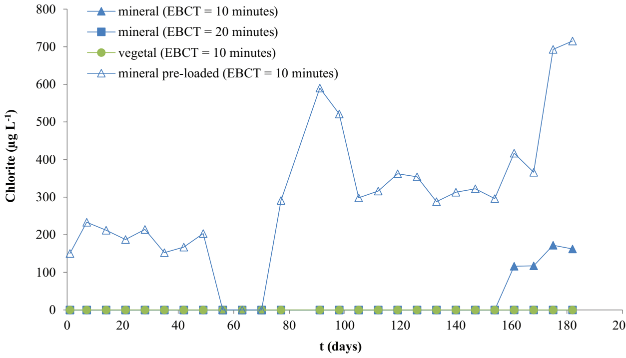

Fig. 3. Residual ClO_2^- concentration in samples collected at the outlet of the carbon columns operating with 10 and 20 min EBCT, in the second column test (C2).

The ClO_2^- concentration at the outlet of the pre-loaded mineral GAC is detected from the first day of operation and ranges between 150 and 600 μg L^{-1}; only after 6 months it exceeds the regulation limit of 700 μg L^{-1}. The comparison between virgin and pre-loaded mineral GACs (both operating with Q = 1 L h^{-1} and contact time of 10 min) agrees with the results of the C1 column test (Fig. 2), since the carbon pre-loading significantly reduces the ClO_2^- removal yield. This result confirms that ClO_2^- removal process loses its efficiency when GAC is pre-loaded with organic matter and specific ions [20].

3.2. Pilot plant at semi-full scale (P)

The residual ClO_2^- concentrations were determined on samples collected at the inlet and outlet of the pilot sand column, and at the outlet of the pilot GAC column (Fig. 4).

The ClO_2^- concentration at the inlet of the pilot sand column is not constant and it is proportional to the ClO_2 dosage employed in the pre-oxidation process: when the dosage is high (0.8–0.9 mg L^{-1}), the ClO_2^- concentration is high of course, but always below the regulation limit of 700 μg L^{-1}. The average ClO_2^- concentration at the inlet of the pilot sand column is 646 μg L^{-1} (maximum 1,042 μg L^{-1} and minimum 411 μg L^{-1}).

Since the ClO_2^- concentration trends at the inlet and outlet of the pilot sand column are similar, it can be stated that the pilot sand filter does not guarantee high ClO_2^- removal

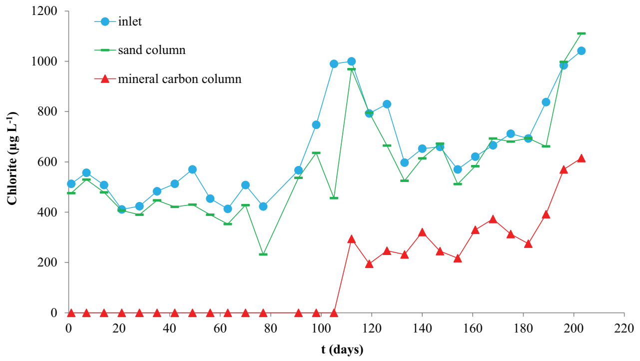

Fig. 4. Residual ClO_2^- concentration in samples collected at the inlet and outlet of the sand column, and at the outlet of the mineral GAC column, both operating with a 5 min EBCT, in the pilot test (P).

yields and even, sometimes, the concentration at the outlet is slightly higher than the one at the inlet. Its average ClO_2^- removal yield is about 11%, the average ClO_2^- concentration at the outlet of the pilot sand column is 579 μg L^{-1} and it varies in the range of 232–1,110 μg L^{-1}.

The pilot GAC column guarantees a complete ClO_2^- removal for 3.5 months and, then, ClO_2^- concentration increases varying between 200 and 400 μg L^{-1}. After 190 days the carbon exhaustion process further increases, since the ClO_2^- concentration at the inlet of the pilot sand column increases up to 800 μg L^{-1}; however, after 200 days the ClO_2^- concentration at the outlet of the GAC column is still below the regulation limit of 700 μg L^{-1}. From 3.5 months until the end of the monitoring period the average ClO_2^- removal yield from the outlet of the pilot sand column to the outlet of the pilot GAC column is close to 55%.

In the first 3.5 months, the ClO_2^- removal is mainly due to the reduction of ClO_2^- to chloride, while after this period the ClO_2^- is removed by the adsorption process on the GAC active sites, which is a slow process that can be observed in the long period [20].

3.3. Comparison between column tests at laboratory scale and pilot column test at semi-full scale

The ClO_2^- concentration at the outlet of the virgin vegetal GAC column at laboratory scale after 5 and 10 min EBCT throughout the column operating period is shown in Fig. 5.

It can be stated that the vegetal GAC column with a 10 min EBCT (C2) ensure a complete ClO_2^- removal during all the monitoring period, while with a 5 min EBCT (C1) the complete removal is registered only during the first month of operation. Then, only with a 5 min EBCT a gradual increase is observed by reaching concentrations up to 470 μg L^{-1}. Therefore, as expected, a lower EBCT implies an acceleration in the carbon breakthrough achievement. This result again agrees with the fact that with a higher water flow, the GAC is more charged by ClO_2^- and, therefore, it rapidly achieves the breakthrough. Moreover, at a low EBCT the predominant ClO_2^- removal process is the reduction of ClO_2^- to chloride, while the adsorption of ClO_2^- on the GAC active sites increases at a higher EBCT [20].

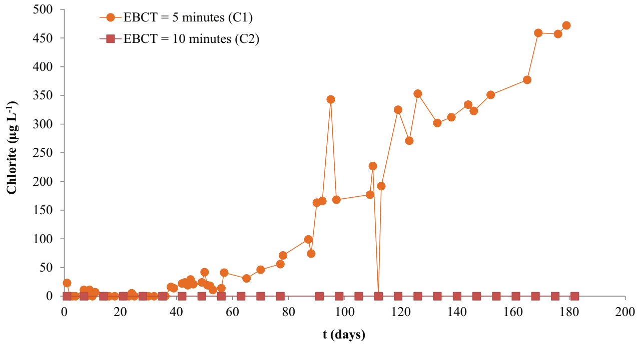

Fig. 5. Residual ClO_2^- concentration in samples collected at the outlet of the virgin vegetal GAC columns operating with 5 and 10 min EBCT, respectively, in the first and second column tests (C1 and C2).

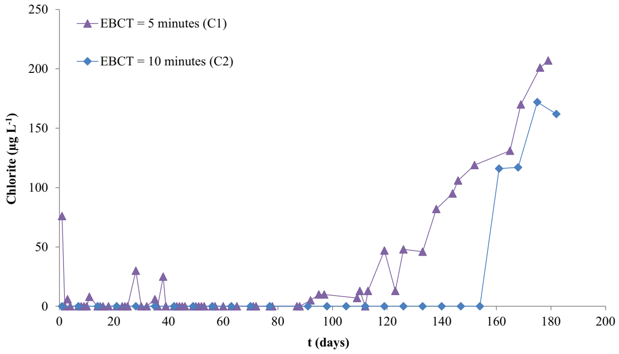

Fig. 6. Residual ClO_2^- concentration in samples collected at the outlet of the virgin mineral GAC columns operating with 5 and 10 min EBCT, respectively, in the first and second column tests (C1 and C2).

The ClO_2^- concentration at the outlet of the virgin mineral GAC column after 5 and 10 min EBCT throughout the column operating period is shown in Fig. 6.

In virgin conditions, the mineral GAC operating with a 10 min EBCT guarantees a complete ClO_2^- removal for a longer period than with a 5 min EBCT. Then, a sharp increase up to 170 μg L^{-1} is observed with a 10 min EBCT, while a gradual increase up to 200 μg L^{-1} is shown with a 5 min EBCT.

The ClO_2^- concentration at the outlet of the pre-loaded mineral GAC column after 5 and 10 min EBCT throughout the column operating period is shown in Fig. 7.

In pre-loaded conditions, the mineral GAC shows an anomalous higher ClO_2^- removal efficiency with a 5 min EBCT (C1) than with a 10 min EBCT (C2). In fact, with a 5 min EBCT the ClO_2^- concentration is always below 200 μg L^{-1}, while with a 10 min EBCT it is higher, reaching values over the regulation limit of 700 μg L^{-1}.

Overall, the virgin GACs, both mineral and vegetal, show a better performance with a 10 min EBCT, while the pre-loading behavior is not completely clear.

The ClO_2^- concentrations after adsorption with the virgin mineral GAC in the small column tests at laboratory scale (C1 and C2) and in the pilot column test at semi-full scale (P) are shown in Fig. 8.

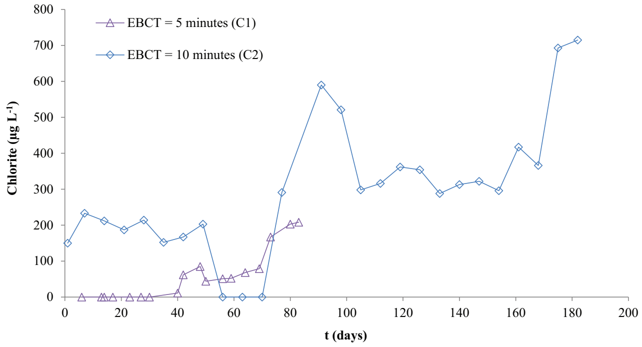

Fig. 7. Residual ClO_2^- concentration in samples collected at the outlet of the pre-loaded mineral carbon columns operating with 5 and 10 min EBCT, respectively, in the first and second column tests (C1 and C2).

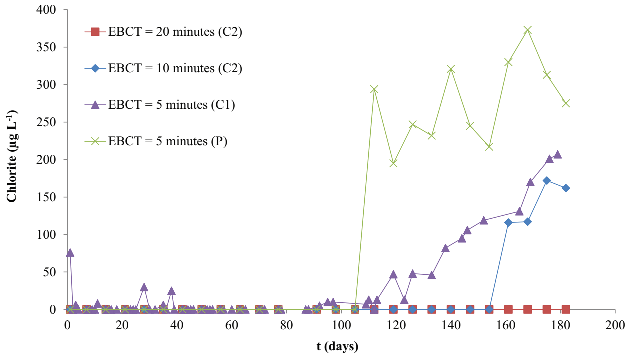

Fig. 8. Residual ClO_2^- concentration in samples collected at the outlet of the virgin mineral GAC columns operating with 5, 10, and 20 min EBCT, in the first and second small column tests (C1 and C2) and in the pilot column test (P).

The results show that with increasing EBCT the ClO_2^- concentration at the outlet of the mineral GAC column decreases; moreover, with a 5-, 10-, and 20 min EBCT a 100% ClO_2^- removal yield is obtained for about 3.5, 5, and 6 months, respectively. This confirms that a lower EBCT implies the carbon breakthrough achievement in a shorter period from the start-up of the column.

Comparing the pilot column (P) with the C1 small column test, both operating with a 5 min EBCT, in the first case (P) the mineral GAC column allows a complete ClO_2^- removal till the 105th day of operation, and in the second case (C1) till the 92nd day. Therefore, the small column tests behavior is significantly representative of the pilot plant performance in terms of breakthrough. However, comparing the laboratory and pilot columns, the ClO_2^- removal behavior changes after the breakthrough achievement. This could be due to chemical and physical factors, such as pore–surface diffusion and internal mass transfer, to the geometrical characteristics of the columns and the column wall effect that influence the hydrodynamic conditions [30].

Overall, as shown by the experimental results of this study, the performance of a full-scale GAC column can be realistically predicted by means of small column tests at laboratory scale and by means of column tests at pilot scale.

4. Conclusions

This paper shows how laboratory- and pilot-scale tests are useful to predict the GAC performance on the ClO_2^- removal in a full-scale DWTP. Different experimental tests were carried out at laboratory scale by means of small columns and at pilot scale comparing a mineral and a vegetal GAC, in virgin and pre-loaded conditions. The results show that the virgin mineral carbon guarantees a higher ClO_2^- removal efficiency than the vegetal one, while in pre-loaded conditions an opposite behavior is observed. Moreover, the carbon pre-loading significantly reduces the ClO_2^- removal.

Small column tests and pilot column test show that a low EBCT implies the breakthrough achievement from the start-up of the GAC column in a short period.

Comparing the two types of tests, column experiments at laboratory scale are significantly representative of the pilot plant performance. Therefore, it can be stated that column tests at laboratory and pilot scale can predict the performance of a full-scale DWTP.

Acknowledgments

The authors would like to thank Centro Veneto Servizi (C.V.S.) SpA, which is the company that manages the Vescovana DWTP (Padova, Italy) studied in this research. Special thanks also go to Hydro-line technical staff that took part in this experimentation.

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