Effectiveness in chlorite removal by two activated carbons under different working conditions: a laboratory study

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ABSTRACT

Activated carbon is used in many drinking water facilities because it can remove a broad spectrum of contaminants (e.g., herbicides, pesticides, heavy metals, etc.) or to replace anthracite coal in dual media filters. In recent years, liquid chlorine has been substituted by chlorine dioxide (ClO_2) because, for instance, it can remove natural organic matter in raw water without formation of harmful disinfection by-products. Interest in chlorine dioxide is due to formation of chlorite (ClO_2^-), which can be potentially toxic for humans. In this study, the authors investigated the applicability of two activated carbons coming from different matrices (coconuts and bituminous) as technology for chlorite removal. The activated carbons were tested at different conditions (virgin and pre-loaded with some substances) in order to simulate full-scale working situations, and their Freundlich isotherms were determined. The results show a good affinity of virgin carbons in chlorite removal (about 80%), but the pre-loading significantly affected the efficiency of the chlorite removal process, reducing it to only 19%. An investigation into the main removal mechanism used by the carbons for chlorite removal was also done. Results show that activated carbons used both reduction and adsorption processes.

Key words | activated carbon, carbon pre-loading, chlorite, Freundlich isotherm

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INTRODUCTION

The progressive increase in pathogens and chemical pollutants in natural water due to human activity requires more and more complex treatments for its purification. More restrictive targets in pollutant removal can be reached with the use of chlorine (e.g., killing bacteria and ammonia removal) but it can lead to the formation of harmful by-products, such as trihalomethanes and haloacetic acids, whose negative effects on human health are reported in many studies (e.g., Lubbers et al. 1984; Yang et al. 2000; Cedergren et al. 2002; Ivancev et al. 2002).

In recent years, liquid chlorine has been substituted with chlorine dioxide (ClO_2), which has become the most common disinfectant in drinking water plants (DWTPs) (Lykins & Griese 1986; Narkis et al. 1995; Ranieri & Swietlik 2010). The main advantages of ClO_2 are the removal of natural organic matter (NOM) without formation of harmful disinfection by-products (DBPs) (Singer 1994; El-Dib et al. 2000; Badawy et al. 2012), the oxidation effectiveness over a wide pH range (3–9) (White 1992; Junli et al. 1997), and the removal of bad odors (White 1992; Edwards & Amirtharajah 1993), iron and manganese (Aieta & Berg 1986; White 1992). Moreover, chlorine dioxide is very effective in killing bacteria and especially in deactivating viruses (Korn et al. 2002).

The dosage of chlorine dioxide in final disinfection has been debated because its use leads to the formation of inorganic DBPs, such as chlorate (ClO_3^-) and chlorite (ClO_2^-). Many authors found that about 50–70% of the chlorine dioxide consumed by oxidation reactions is converted into chlorite accordingly to the water characteristics (Aieta & Berg 1986; Werdehoff & Singer 1987; Singer 1994; Minear

& Amy 1996; Schmidt *et al.* 2000; Gordon 2001; Sorlini & Collivignarelli 2005).

The International Agency for Research on Cancer has concluded that chlorite is not classifiable as carcinogenic to humans. The primary and most consistent finding arising from exposure to chlorite is oxidative stress resulting in changes in the red blood cells in laboratory animals and, by analogy with chlorate, in humans exposed to high doses in poisoning incidents. Studies with human volunteers for up to 12 weeks did not identify any effect on blood parameters at the highest dose tested, 36 µg/kg body weight per day (WHO 2011). The WHO guideline values for chlorite and chlorate (0.7 mg/L each) are designated as provisional because the use of chlorine dioxide as disinfectant may result in chlorite and chlorate guideline values being exceeded. European Council Directive 98/83/EC does not indicate a limit value for chlorite while the current Italian regulation on drinking water (Legislative Decree 2nd February 2001 n. 31) introduced a maximum concentration for chlorite of 0.2 mg/L, subsequently increased to 0.7 mg/L by the Decree of the Ministry of Health of 5th September 2006. In the case of preoxidation with chlorine dioxide, specific treatments should be applied in order to remove chlorite before water distribution. Among the available techniques, the addition of reducing agents such as sulfur dioxide and sodium sulfite (Gordon *et al.* 1990; Dixon & Lee 1991; Vel Leitner *et al.* 1992), ferric salts, e.g., ferrous chloride and ferrous sulfate (Aieta & Berg 1986; Griese *et al.* 1991, 1992; Katz & Narkis 2001), can be applied but additional costs for water treatment must be considered. An alternative solution is removal with granular activated carbon (GAC), which is generally applied in DWTPs for other purposes, e.g., the removal of organic compounds and organic micropollutants. Many authors (Dixon & Lee 1991; Gonce & Voudrias 1994; Vel Leitner *et al.* 1996; Ebie *et al.* 2001; Sorlini & Collivignarelli 2005) studied the applicability of GAC for chlorite removal, but the mechanisms are not very clear and adverse results were found depending on GAC properties, empty bed contact time (EBCT), water pH, and ClO_2^- concentration. Moreover, the removal mechanisms of chlorite by GAC were investigated but with contrasting findings; Voudrias *et al.* (1983) observed that if the removal mechanism of chlorite is mainly due to reduction on the activated carbon surface, chlorides are released in water and the yield of removal is about 20–30%

(Vel Leitner *et al.* 1996). In contrast, if the main mechanism is the adsorption onto the carbon active sites, no chlorides are found in water after the treatment with GAC. Dixon & Lee (1991) also observed that GAC, pre-loaded with NOM, has a very low chlorite removal efficiency (15–20%); however, an increase in contact time (EBCT from 2 to 10 minutes) increases the removal efficiency from 30 to 80%.

Removal mechanisms can be investigated both at laboratory scale and pilot/full scale. Generally, batch tests at laboratory scale, such as Freundlich isotherm and rapid small-scale column tests (RSSCTs), exhibit different adsorption capacity than full-scale data. One of the limitations of the Freundlich isotherm test is that it should only be used to model the equilibrium data in the concentration range for which it is developed and therefore its results may not be representative of the GAC performance in the full-scale plant where steady-state conditions are not guaranteed. Moreover, RSSCTs generally exhibit more adsorption capacity than full-scale data (Crittenden *et al.* 2012; Chowdhury *et al.* 2013). These tests are widely utilized because they allow useful information to be quickly obtained regarding the ability of the activated carbon for the removal of target contaminants. Moreover, in order to extend the experimental results into design parameters (e. g., system size, EBCT, carbon usage rates, hydraulic retention time), continuous flow tests (e.g., column studies or pilot plants) should be conducted. An example of this approach based on the combination of batch followed by continuous flow tests is reported in Sorlini *et al.* (2015).

In this study, the authors investigated the applicability of activated carbon for chlorite removal. For this purpose, two GACs of vegetal and mineral origin (coconuts and bitumen) were tested in batch conditions (Freundlich isotherms), both on virgin and pre-loaded carbons. Moreover, the main reduction or adsorption removal mechanism of chlorite was investigated.

MATERIALS AND METHODS

Virgin activated carbons

GACs from different origins (coconut and bitumen, called vegetal and mineral, respectively) were tested. A total amount of 100 kg of each activated carbon was available

and representative amounts for laboratory tests were sampled according to UNI-ISO 11648-2:2008. Powdered activated carbons (PACs) were obtained by grinding GACs to fine particles (95% of the mass smaller than U.S. 325-sieve). Before the experimental activity, a complete characterization of activated carbons was conducted (Table 1).

Specific surface area and pore size distribution

Specific surface area (m^2/g) was determined by nitrogen multilayer adsorption (conducted at 77 K) measured as a function of relative pressure using a fully automated analyzer (Kelvin 1042, Costhech Instruments) and the value was calculated according to the Brunauer–Emmett–Teller (BET) equation. During the tests, the pore size distribution was determined by applying two models: the Dubinin–Radushkevich equation for micropore volume and the Barrett–Joyner–Halenda (BJH) analysis for meso and macropore volume (according to Barrett et al. 1951).

Reagents and GAC pre-loading procedure

Two different types of water were used in the tests: deionized and bi-distilled water (Carlo Erba reagents). The

desired amount of chlorite in the water (1.0 mg/L) was obtained by dosing a solution of 31% v/v sodium chlorite ($NaClO_2$) in deionized water and its initial and final concentration in the solution was measured by ionic chromatography (Metrohm Compact IC 761). To simulate the saturation of the various pore fractions, three different solutions were used for PAC pre-loading. The chemicals used for this were chosen on the basis of their molecular diameter (i.e., iodine, phenol, methylene blue, and molasses) or to simulate a specific contaminant commonly present in raw water (i.e., humic acid for NOM). In this way, phenol (molecular diameter of about 0.7–0.8 nm) and iodine (molecular diameter of 1.0 nm) were used to pre-load micropores while methylene blue (molecular diameter of 1.5 nm) and molasses (molecular diameter of 3.0 nm) were used for mesopores. The pore dimensions were considered according to the International Union of Pure and Applied Chemistry (IUPAC) classification.

The first pre-loading solution was obtained by mixing iodine (75.0 g/L, Sigma–Aldrich reagent), methylene blue (20.0 g/L, Sigma–Aldrich reagent), and molasses (Sigma–Aldrich reagent); the second one was obtained by adding 10.0 mg of humic acids in granular form (Sigma–Aldrich

Table 1 | Properties of activated carbons

Properties	Analytical methods	M.U.	Vegetal	Mineral
Origin	–	–	Coconuts	Bitumen
Volatile solids	ASTM D5832-98	%	3.9	1.3
Total ashes	ASTM D2866-11	%	2.5	12.3
Bulk density	ASTM D7481-09	kg/m^3	457	428
Apparent density	ASTM D2854-09	kg/m^3	491.0	463.0
pH	ASTM D3838–05	–	9.4	9.1
Coefficient of uniformity[a] (D_{60}/D_{10})	ISO 13320:2009	–	1.6	1.6
Iodine number	AWWA B600-10	mg/g	1204	971
MBV	CEFIC 1986	g/100g	29	26
BET specific surface area	BET	m^2/g	1206.56	1037.86
Total pores volume	BJH analysis	mm^3/g	560.6	552.6
Micropores volume[a] (<2 nm)	Dubinin–Radushkevich equation	mm^3/g	393.6	207.8
Mesopores volume[a] (2–50 nm)	BJH analysis	mm^3/g	41.9	123.2
Macropores volume[a] (>50 nm)	BJH analysis	mm^3/g	125.1	221.6

[a]According to IUPAC classification.

reagent). The third solution was obtained by spiking 2.0 g/L of phenol (Sigma–Aldrich reagent) (AWWA 1999). During the activated carbon pre-loading process, a beaker was filled with 500 mL bi-distilled water and 4.0 g of each pulverized carbon was added. The water was kept in stirring conditions (100 rpm) until PAC saturation was reached (assumed when no variation in methylene blue value (MBV) and iodine index were observed). At the end of the pre-saturation process, the activated carbons were filtered on a No. 2 Whatman filter paper (filtration in the 8 μm particle size range). Finally, the carbons were dried at ambient temperature (only in the case of pre-loading with humic acids were the PACs washed with bi-distilled water before drying).

Freundlich isotherms

The adsorption isotherm represents the relation between the amount of adsorbate removed from the liquid phase by unit mass of adsorbent at a fixed temperature. The equilibrium studies were performed calculating the Freundlich isotherm according to ASTM D3860-98: 1.0 g of both pulverized carbons (virgin and pre-loaded) was added in a flask containing 1 L of deionized water forming a carbon stock suspension. Eight aliquots of 500 mL of deionized water containing 1.0 mg/L of chlorite were spiked with 1.0, 2.5, 5.0, 7.5, 10.0, 25.0, and 50.0 mL of stock suspension at regular intervals (the last solution – the eighth – was used as control). Each flask was kept stirring for a fixed contact time (5 or 10 minutes). After this time, PAC was removed from the solution by filtration on No. 42 Whatman filter paper (filtration in the 2.5 μm particle size range) and the chlorite concentration in the water was analyzed through the ionic chromatograph. The tests were performed at 298 K.

The Freundlich isotherm was calculated in linear form, as follows (1):

$$\text{Log}\,(X/M) = \text{Log}\,(K) + 1/n\,\text{Log}\,(C) \tag{1}$$

where X/M = ratio between chlorite adsorbed [mg] and weight of carbon [g]; C = chlorite concentration in the solution at equilibrium [mg/L]; K = Freundlich adsorption capacity parameter [mg/g] (Van Bladel & Moreale 1977); n represents the parameter characterizing quasi-Gaussian

energetic heterogeneity of the adsorption (Bansal & Goyal 2005); the ratio $1/n$ is also called the Freundlich adsorption intensity parameter [unitless] (Van Bladel & Moreale 1977).

Investigation of the removal mechanisms

Many authors (Voudrias *et al.* 1983; Vel Leitner *et al.* 1996) reported that chlorite can be removed from water through a chemical process (reduction) that occurs between the carbon active sites (*C) and chlorite. In this case, the process is controlled by the reaction (2) and chloride and carbon dioxide are found as final products

$$\text{ClO}_2^- + *\text{C} \rightarrow \text{Cl}^- + \text{CO}_2 \tag{2}$$

To investigate chloride (Cl^-) production in the water, two tests were performed. The aim of the first test was to estimate the amount of chloride which can be naturally released by the virgin carbon in water, while the second test was aimed at investigating chloride production due to the possible reduction process. In both experiments, 1 L of bi-distilled water (spiked with 1.0 mg/L of chlorite in the second test) was kept in contact with 50.0 mg of dried virgin PAC (both mineral and vegetal) and kept stirred (100 rpm) for 54 hours. During the tests, at different intervals, the chloride concentration (and chlorite in the case of spiked water) was measured. The tests were performed at 298 K.

RESULTS AND DISCUSSION

Activated carbons

In Table 1, the main characteristics of tested activated carbons are reported.

Both activated carbons showed high value of the coefficient of uniformity equal to 1.6, indicating a good uniformity, similar to the value reported by Snoeyink & Summers (1999). The main differences between the activated carbons were represented by the total ash and volatile solid content, iodine number, BET specific area, and pore distribution. The vegetal carbon presented higher volatile solids

content (3.9 vs. 1.3%, the percentages refer to the initial mass) and lower amount of total ash (2.5 vs. 12.3%). Moreover, the vegetal carbon showed higher values of the adsorption indexes (MBV and iodine index). Regarding the pore distribution (according to IUPAC classification), the higher micropore volume was observed for the vegetal carbon (393.6 vs. 207.8 mm^3/g) while the mineral one showed the higher amount of macro and mesopores (221.6 mm^3/g and 123.2 mm^3/g, respectively).

Equilibrium studies

The equilibrium studies were conducted testing 5 and 10 minutes as contact time. The best results on chlorite removal were observed for 10 minutes (data presented in this paper).

In Table 2, the PAC removal efficiencies are reported while in Figures 1 and 2 the Freundlich isotherms are represented.

Virgin PACs

As shown in Table 2, chlorite removal efficiencies of both virgin PACs increased from 4.0 to 80.8% by increasing the activated carbon dosage from 1.0 to 50.0 mg/L. The X/M ratio dropped from 18.50 to 7.20 mg/g for the vegetal carbon and from 21.50 to 7.72 mg/g for the mineral one.

Low values of the adsorption intensity parameters ($1/n$) were obtained for both PACs (see Figures 1 and 2); this means that the adsorption bonds are strong and the activated carbons have a good affinity on chlorite removal, accordingly with the value of Log(K) coefficients (1.189 and 1.214 for vegetal and mineral PAC, respectively). Good values of linear correlation coefficient (R^2) were found confirming that the adsorption model is successfully predicted by the Freundlich model ($R^2 = 0.63$ and 0.76 for vegetal and mineral carbon, respectively).

Regarding the influence of the physico-chemical characteristics of activated carbons, it seems that the mesoporous fraction affects positively the removal efficiency of the chlorite; in fact, the results show that the mineral carbon, characterized by a greater mesoporous fraction, obtains a slightly higher removal efficiency if compared to the vegetal one (80.8% vs. 78.2%, respectively). This result is in accordance with the findings of Sorlini *et al.* (2015), where it is shown that the microporous fraction more easily removes low-molecular weight compounds.

Pre-loaded PACs

Table 3 reports the duration of the pre-loading process and the values of the adsorption indexes of the PACs at the end of the pre-loading process. Different contact times

Table 2 | Chlorite removal efficiencies obtained by the PACs at different carbon dosage and pre-loading conditions (virgin and pre-loaded). Chlorite initial concentration 1.0 mg/L

| Activated carbon type	Weight of PAC [mg]	Virgin X/M [mg/g]	Chlorite removal efficiency [%]	Iodine, methylene blue, molasses X/M [mg/g]	Chlorite removal efficiency [%]	Humic acids X/M [mg/g]	Chlorite removal efficiency [%]	Phenol X/M [mg/g]	Chlorite removal efficiency [%]
Vegetal	1.0	18.50	4.0	29.50	6.4	6.00	1.1	6.25	1.4
	2.5	16.20	8.8	23.00	12.5	5.00	2.3	4.79	2.7
	5.0	11.70	12.7	30.80	33.5	4.60	4.3	3.85	4.3
	7.5	11.20	18.2	26.93	44.0	3.87	5.4	3.68	6.1
	10.0	12.35	26.8	24.75	53.9	4.85	9.1	4.06	9.0
	25.0	11.92	64.7	12.30	66.9	3.10	14.5	3.23	17.9
	50.0	7.20	78.2	7.01	76.3	2.45	22.9	2.67	29.6
Mineral	1.0	21.50	4.5	16.50	3.7	7.00	1.2	5.26	1.2
	2.5	13.20	6.9	14.60	8.1	9.60	4.1	4.42	2.5
	5.0	14.60	15.3	17.90	19.8	9.20	7.8	3.47	3.9
	7.5	13.53	21.3	14.73	24.5	7.27	9.2	2.53	4.2
	10.0	12.65	26.5	15.70	34.8	7.25	12.3	3.79	8.4
	25.0	10.78	56.4	11.18	62.0	2.20	33.8	2.44	13.6
	50.0	7.72	80.8	6.49	72.0	2.09	42.2	1.74	19.3
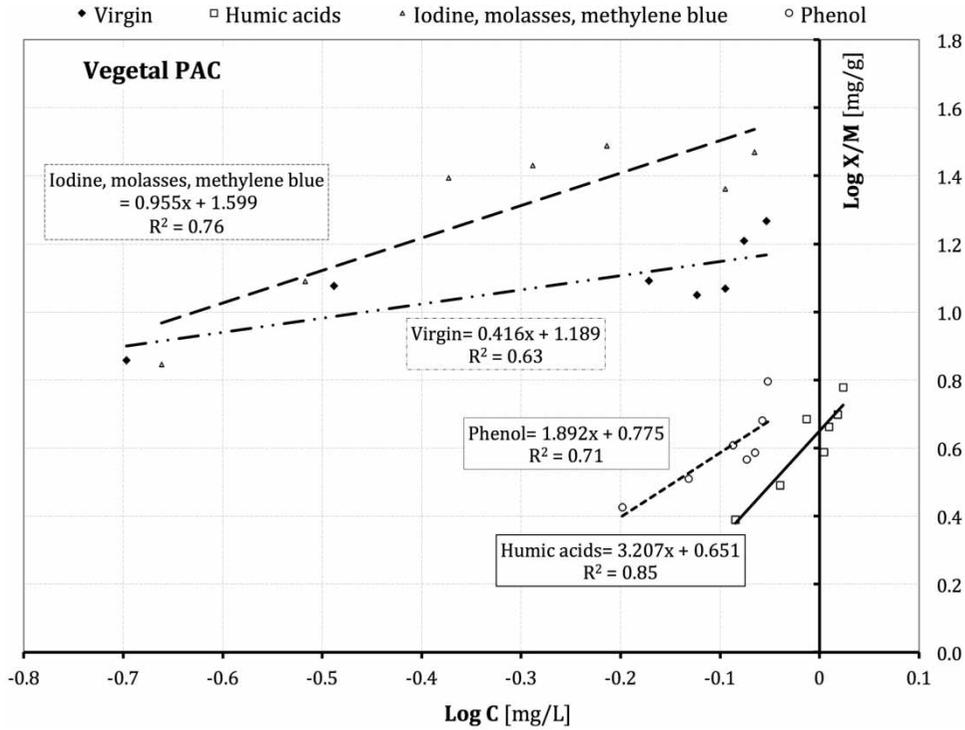
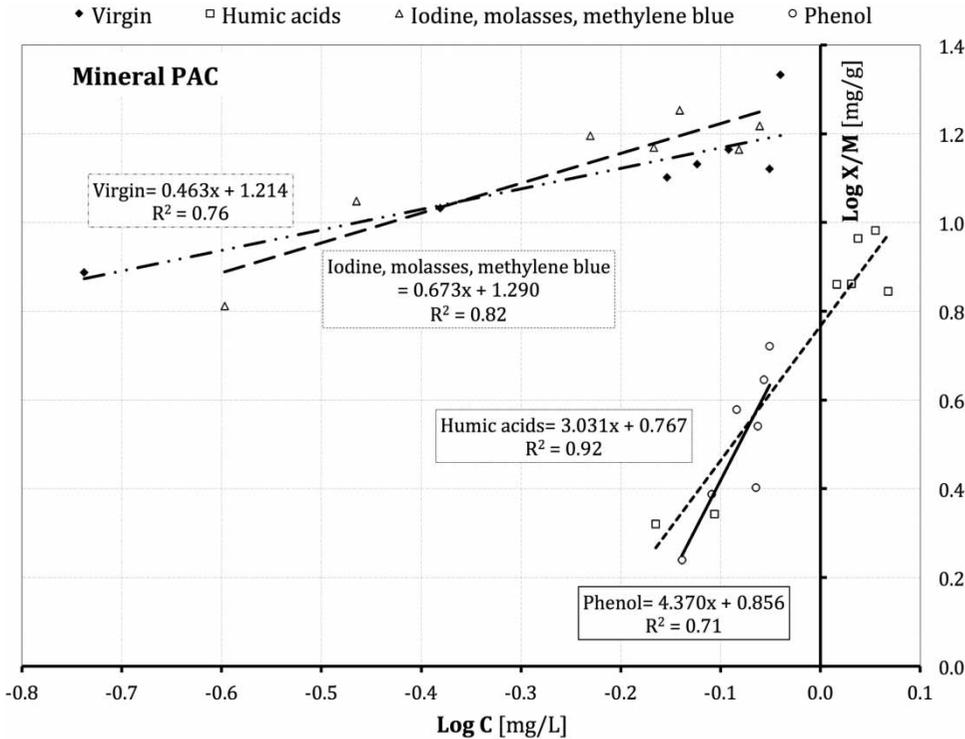**Figure 1** | Freundlich isotherms of vegetal activated carbon (virgin and pre-loaded).

Figure 2 | Freundlich isotherms of mineral activated carbon (virgin and pre-loaded).

Table 3 | Characteristics of PACs at the end of pre-loading period and its duration

Activated carbon	Pre-loading solution	Pre-loading time [d]	Iodine index [mg/g]	MBV [g/100 g]
Vegetal	Iodine, methylene blue and molasses	10	<550	10
Mineral			<550	5
Vegetal	Humic acids	22	1,075	24
Mineral			835	20
Vegetal	Phenol	6	511	2
Mineral			546	7

between the activated carbon and the pre-loading solutions were needed depending on the type of PAC and on the pre-loading solution.

It can be observed that the first pre-loading solution (containing iodine, methylene blue, and molasses) could effectively pre-load the carbon that, at the end of the pre-loading process, showed low values of MBV and iodine index. Apparently, the pre-loading process performed using humic acids and phenol did not seem to be effective; in fact, MBV and iodine indexes shows values similar to the virgin activated carbons.

This is probably due to the low solubility of humic acids and phenol in water, at ambient temperature, that favored the formation of a film on the activated carbon surface thereby inhibiting the adsorption of these molecules.

In Table 2, the removal efficiencies of carbon pre-loaded with a mix of iodine, methylene blue, and molasses are shown. Comparing the iodine number and MBV of pre-loaded carbons (Table 3) with the virgin ones (Table 1), a significant reduction can be observed, confirming the saturation of meso-micropores. The results indicate that the pre-loaded operation reduces the removal of chlorite of both carbons; however, an increase of the chlorite removal was obtained increasing the carbon dosage from 1.0 to 50.0 mg/L. The maximum removal yield was obtained with the vegetal carbon (76.3%) while a lower removal was observed with the mineral PAC (its removal efficiency dropped to 72.0%. This behavior can be due to the different PAC specific surface area (1,037.86 m^2/g vs. 1,206.56 m^2/g, mineral and vegetal activated carbon, respectively) and pore

size distribution (the mineral PAC showed higher meso-pores volume – 123.2 vs. 41.9 mm^3/g and lower micropores volume – 207.8 vs. 393.6 mm^3/g if compared to the vegetal one), parameters that could affect chlorite adsorption. Also, in this case, the PACs are able to remove chlorite but cannot create stronger adsorption bonds, as indicated by the values of $1/n$ coefficient proximally to 1 (0.96 and 0.67 for vegetal and mineral PAC, respectively, as reported in Figures 1 and 2). This hypothesis is consistent with the $Log(K)$ values (1.599 and 1.290 for vegetal and mineral PAC, respectively). Also, in this case, the adsorption model is successfully predicted by the Freundlich model, as confirmed by the high values of linear correlation coefficient ($R^2 = 0.76$ and 0.82 for vegetal and mineral PAC, respectively).

The removal efficiencies of the carbons pre-loaded with humic acids are summarized in Table 2. Both the activated carbons show a high reduction of chlorite removal; the lowest value was obtained by vegetal carbon (22.9%) even though the mineral one reaches only 42.2%; also, in this case, the removal efficiencies increased with increasing the activated carbon dosage from 1.0 to 50.0 mg/L. Low X/M ratio values (2.45 and 2.09 at the maximum dosage of vegetal and mineral PAC, respectively) were found, meaning that the removal efficiency of both PACs is strongly affected by the initial chlorite concentration and the higher removal efficiency could be reached by increasing the carbon dosage. Probably, the lower removal efficiency reached by vegetal PAC could be attributed to its lower volume of macropores (125.1 vs. 221.6 mm^3/g); in fact, these pores play an important role in the adsorption process (they are the gates to micropores) and, if they are obstructed by the humic acid molecules, chlorite cannot be transported within the micropores and the removal process cannot be completed (such as the reduction process because chlorite cannot react with the carbon surface). This is in agreement with the findings of Kilduff et al. (1996a, b), reporting that the molecular sieving mechanism (i.e., the ability of the carbon pores to select molecules of varying dimension) affects the adsorption of humic acids. The values of $Log(K)$ parameter (0.651 vs. 0.767 for vegetal and mineral carbon, respectively) do agree with the findings of Lee et al. (1981), who observed that the

adsorption constant (K) increased with increasing mesopores volume. Moreover, it seems that the vegetal carbon can create adsorption bonds weaker than the mineral one, as indicated by the $1/n$ values (3.207 and 3.031, respectively) reported in Figures 1 and 2. High values of the linear correlation coefficients were found ($R^2 = 0.85$ and 0.92 for vegetal and mineral PAC, respectively) confirming that the adsorption model is successfully predicted by the Freundlich isotherm.

The worst chlorite removal yields were obtained by both PACs pre-loaded with phenol; in fact, with the maximum dosage of activated carbon (50.0 mg/L) chlorite removal yields were 19.3 and 29.6% for mineral and vegetal PAC, respectively. Comparing the X/M ratio, the vegetal PAC shows the higher values (2.67 vs. 1.74 of mineral one) meaning that a significant amount of contaminant can be adsorbed by this carbon. Also, in this case, the adsorption process is successfully predicted by the Freundlich model, as confirmed by the good values of the linear correlation coefficients ($R^2 = 0.71$, both PACs). In this experiment, higher values of $1/n$ coefficients were achieved (1.892 and 4.370 for vegetal and mineral PAC, respectively) meaning that no strong adsorption bonds can be created (especially in the mineral PAC); the mineral PAC shows a better adsorption affinity if compared to the vegetal one (Log $(K) = 0.856$ and 0.775 for mineral and vegetal PAC, respectively).

Investigation of chlorite removal mechanisms

To better investigate chlorite removal processes, chloride concentrations at different times in two solutions (bi-distilled and spiked water) were monitored as an increase in the chloride concentration should be observed in the solution if the main removal mechanism of chlorite is the reduction (Voudrias *et al.* 1983; Vel Leitner *et al.* 1996).

Figure 3 represents the trend of chlorides (Cl^-) released by 50.0 mg of PACs in bi-distilled water without chlorite; in this case, the release of chlorides in the solution is probably due to the residues of chemical agents used during the activation process (e.g., zinc chloride). As represented in Figure 3, the PACs released a significant amount of chlorides instantly while in a further 24 hours they decreased and again increased in the solution. At 30 hours from the beginning of the test, the vegetal activated carbon reached, substantially, asymptotic value (0.080 mg) while the mineral one still released a significant amount of chlorides increasing from 0.100 to 0.140 mg (asymptotic value) at 48 hours.

The initial peak release of chlorides in bi-distilled water was due to their high solubility while their decrease with time was probably due to their partial adsorption onto carbon active sites (Pelekani & Snoeyink 1999).

Figure 4 reports the results of the second test, carried out with bi-distilled water spiked with chlorite at a concentration of 1.0 mg/L, in contact with 50.0 mg of virgin
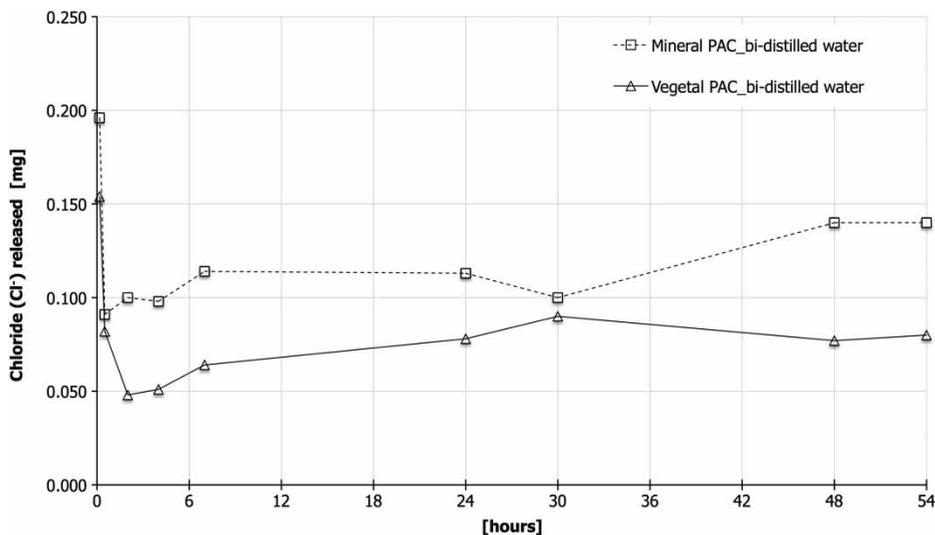

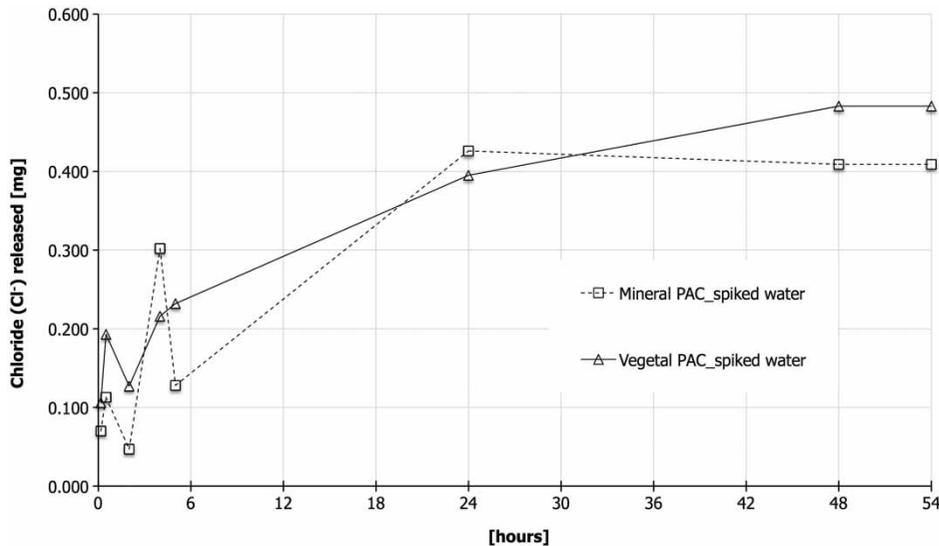Figure 3 | Chlorides released in bi-distilled water by the PACs.

Figure 4 │ Chlorides released in spiked bi-distilled water (chlorite initial concentration: 1.0 mg/L) by the PACs.

PAC. Chloride initial concentration in bi-distilled water was negligible. In this case, a lower amount of chlorides were found for both PACs at the beginning of the test (0.070 mg and 0.106 mg for mineral and vegetal PAC, respectively) and a steady increase during the test was observed. The highest release of chlorides in the solution was reached by the PACs after 48 hours (0.483 mg and 0.409 mg for vegetal and mineral, respectively, which represents the asymptotic values) and no difference was observed in the further 6 hours (54 hours).

The amount of chloride due to the reduction process was estimated as the difference between the amount of chlorides found in the solution at the end of the tests (both with bi-distilled and spiked water) and the chlorides released in bi-distilled water through the following equation (Equation (3)), where $[Cl^-]_{red}$ is the amount of chloride due to reduction [mg]; $[Cl^-]_{bi\text{-distilled}}$ is the amount of chloride found in the bi-distilled water after 54 hours [mg], and $[Cl^-]_{spiked}$ the amount of chloride found in the spiked water after 54 hours [mg].

$$[Cl^-]_{red,} = [Cl^-]_{bi-distilled} - [Cl^-]_{spiked} \qquad (3)$$

The amounts of chlorides produced were 0.406 mg and 0.269 mg for the vegetal and mineral carbons, respectively, suggesting that removal process for vegetal carbon is the combination of two mechanisms (reduction and adsorption)

while the adsorption seems to predominate for the mineral one.

This is consistent with the results obtained in the adsorption tests carried out with PACs pre-loaded with phenol. In this test, it could be assumed that no sieving effect due to the pre-loading substances occurred so all pore fractions were saturated allowing evaluation of the contribution of the reduction mechanism. In this test, the mineral activated carbon obtained a higher value of $1/n$ (4.370 vs. 1.892) indicating that its removal capacity tends to be strongly dependent on the amount of PAC. It means that the adsorption mechanism seems to be negligible and a weak reduction process occurs. Similar analysis can be done for the vegetal PAC for which the higher chlorite removal yield (29.6 vs. 19.3%) is due mainly to the reduction mechanism.

CONCLUSIONS

In this study, the authors investigated the applicability of activated carbon for chlorite removal in drinking water. For this purpose, two activated carbons originated by two different raw materials (coconuts and bitumen) were tested in batch conditions in order to determine the Freundlich isotherms both in virgin and pre-loaded conditions (the pre-loading was carried out with three different solutions: a

mix of iodine, methylene blue, and molasses; humic acids and phenol). The results show that both virgin carbons are effective in removing chlorite and high removal efficiencies were obtained (80.8% vs. 78.2% for the mineral and vegetal, respectively). The lesser removal efficiency of the vegetal PAC can probably be related to the higher content of micropores, responsible for the removal of low-molecular weight compounds. The pre-loading of PACs with a mix of iodine, methylene blue, and molasses did not affect significantly their chlorite removal capacity. The lowest removal efficiencies were obtained by pre-loading the activated carbons with phenol (29.6% for vegetal and 19.3% for mineral). The mineral PAC produced the lowest amount of chloride (0.269 vs. 0.406 mg of vegetal) meaning that the main chlorite removal mechanism could be the adsorption which is hampered if the micropores are occluded. This result was confirmed by the tests performed with humic acids, that were not completely adsorbed into the PAC pores and that produced a thin layer on the PAC surface. This layer had probably partially inhibited both the removal processes, especially the reduction (removal efficiencies obtained: 22.9% and 42.2% for vegetal and mineral PAC, respectively). Finally, it must be highlighted that the so-called molecular sieve effect (i.e., the ability of the carbon pores to select the molecules of different dimensions) could not be excluded by pre-loading PACs with humic acids, so to better understand chlorite adsorption mechanism under this pre-loading condition, the aperture and cavity of the pores could be investigated because they play an important role in the adsorption mechanism.

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