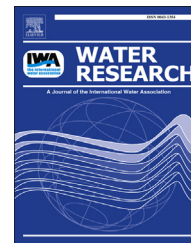


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Phenolic carbon tailored for the removal of polar organic contaminants from water: A solution to the metaldehyde problem?

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ABSTRACT

Current water treatment technologies are inefficient at treating water contaminated with metaldehyde, an 8-member cyclic tetramer of acetaldehyde widely used as a molluscicide in large-scale agriculture and in gardens, and which has been frequently observed to breach European regulatory limits in the UK due to its high solubility and frequent use. Here, we examine the controls on metaldehyde adsorption onto activated phenolic carbon, namely the influence of activation degree, pore size distribution, particle size, point of zero charge and surface functionalisation, by synthesising “tailored” carbons from phenolic resin. Metaldehyde adsorption has been found to be independent of specific surface area (S_{BET}), which is highly unusual for an adsorption process, and is favoured in carbons with (a) high microporosity with narrow pore size distribution, (b) presence of mesopores which allow efficient diffusive transport, and (c) an absence of negatively charged functional groups. The maximum adsorption capacity of the phenolic resin-derived carbons, tested at an elevated (i.e. exceeding environmental levels) water concentration of 64 mg metaldehyde/L, was 76 mg metaldehyde/g carbon compared with 13 mg metaldehyde/g carbon in industrial granular activated carbon (GAC). The phenolic resin-derived carbons and GAC showed similar adsorption kinetics with maximum metaldehyde uptake occurring within 30 min under batch adsorption conditions, although adsorption isotherms indicate much stronger adsorption of metaldehyde on the phenolic resin-derived carbons. Adsorption efficiency for metaldehyde was maintained even in the presence of high background concentrations of organic matter and inorganic salts, indicating the potential utility of these “designer” carbons in waste and/or drinking water treatment.

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1. Introduction

The environmental objectives of the EU Water Framework Directive (WFD) (2000) seek to prevent the deterioration of ground and surface water bodies, and achieve good ecological and chemical status in water courses within the EU Member States by 2015 (Council of the European Communities, 2000). This requires the management of a range of chemicals in the environment, including pesticides, and their supply to water courses. In addition, within the Drinking Water Directive, relatively stringent concentration limits for pesticides have been adopted for drinking water (Council of the European Communities, 1998). However, given the diversity of situations in the various regions of the Community Member states and the technological limitations of many current water purification processes, certain contaminants are allowed to deviate from relevant directives in specific areas if they have been granted with a derogation; which is valid for a limited period of time when required standards cannot be met for particular contaminants and such contamination does not constitute a danger to human health (Council of the European Communities, 1998). Metaldehyde, 2,4,6,8-tetramethyl-1,3,5,7-tetraoxacyclooctane, is one such contaminant, which is inefficiently treated in current wastewater treatment plants (WWTPs) (House of Commons, 2011; Water UK, 2013). It is commonly used as a molluscicide in agriculture and domestic gardening to control snails and slugs, and its large-scale application provides a potential contamination issue in areas where long wet seasons require the control of these plant pests (Bonton et al., 2012; Fabro and Varca, 2012). For example, in the period 2008–2011, 1298 tonnes of metaldehyde were used across the UK, and 4770 tonnes have been used since 1990 (FERA, 2013).

Metaldehyde is soluble in water, with a solubility limit of 0.2 g per litre and log P of 0.12 (both parameters measured at 20 °C and at pH 5, 6.5, 7.2 and 9, European Food Safety Authority, 2010), and has high mobility in the aqueous environment and low affinity for suspended particulate matter. In terms of its stability, 50–78% of metaldehyde was observed to be degraded to CO₂ within 60 days of its application to aerobic soil, but it exhibited higher persistence, with mineralization of just 10% after 45 days, in an anaerobic soil (European Food Safety Authority, 2010). Metaldehyde's stability, high mobility in soil, and solubility in water under typical environmental conditions implies that run-off from treated land provides an uncontrolled input of contamination (European Food Safety Authority, 2010). Furthermore, since rain dissolves the pellets through which metaldehyde is applied, the molluscicide therefore has to be reapplied after rainy periods, which compounds the environmental problem. The current maximum application rate of the molluscicide is 700 g metaldehyde/ha/calendar year in the UK (The Metaldehyde Stewardship Group, 2013). Since 2007, metaldehyde has been detected in surface waters and in some drinking waters across the UK occasionally well above the standard levels set by the Drinking Water Directive (0.1 µg/L) (Council of the European Communities, 1998, 2000; Water UK, 2011, 2013; Bristol Water, 2012). For instance, during the period 2008–2011, the water industry measured concentrations of metaldehyde up to 1.08 µg/L in

some Yorkshire rivers (UK), with peak values more generally ranging between 0.4 and 0.6 µg/L and occurring during October–December (Kay and Grayson, 2013). While much published data refers to the UK, the problem is much wider than in the UK only: in a study where pesticides were monitored periodically in ponds in North eastern France (5 sites located in the Moselle river basin) over the period 2007–2009, metaldehyde was detected in more than 50% of the samples at concentrations ranging between 0.03 and 6.98 µg/L (Lazartigues et al., 2012). Metaldehyde is used widely in other regions beyond NW Europe (e.g. Gavin et al., 2012; Zhongguo et al., 2013). Therefore, water can potentially be contaminated in these areas, although concentrations of metaldehyde in surface water in these regions have not been reported to date (to the knowledge of the authors).

The maximum reported concentration of metaldehyde in UK (treated) drinking water is just above 1.03 µg/L; detected in November 2007 and in December 2008 (Water UK, 2013). These contamination levels do not imply an immediate health risk since the likely intake of metaldehyde is well below the acceptable daily intake (0.02 mg metaldehyde/kg body weight) (Water UK, 2011), but they clearly breach regulatory limits.

The environmental problem posed by metaldehyde is also a challenge for the scientific community, who together with water utilities and with the support of the European Commission, are studying strategies for its removal and the removal of similar highly polar contaminants (Water UK, 2013). Removal by adsorption during tertiary treatment of water, typically using activated carbons, is one of the few viable methods to purify water contaminated with polar contaminants which show limited reactivity with oxidising agents (Teixidó et al., 2011), or where their degradation is affected by background organic matter (Autin et al., 2012). When the organic “skeleton” of the contaminant however is small, as is the case for molecules such as acrylamide, geosimine, 1,1,1-trichloroethane, methyl tert-butyl ether (MTBE) and metaldehyde, the interaction with conventional (activated) carbon will not be strong, hence tertiary treatments involving granular activated carbon (GAC) are relatively ineffective. Recent work however has suggested that “designer” activated carbons (where surface charge and porosity are controlled or “tailored” to target specific groups of contaminants) may have significant potential in the targeted removal of problem and emerging water contaminants (Ragan et al., 2012). Here, we examine the mechanisms governing the uptake of metaldehyde on activated carbon, and synthesise optimal (“tailored”) carbon structures to improve metaldehyde adsorption and maximise its removal from surface, waste and drinking waters.

2. Materials and methods

2.1. Materials

Metaldehyde (CAS 9002-91-9, analytical grade) and 2-chloro-4-ethyl-d₅-amino-6-isopropylamino-1,3,5-triazine (D₅-atrazine) (CAS 163165-75-1, 99% purity) were from Sigma Aldrich (UK). Granular Activated Carbon (GAC) was sourced from Anglian Water, a major UK water utility. Microporous powdered

activated carbons (PAC), which had 8–15 μm particle size, were obtained from three major carbon producers: Picactiff EPII 8/15, coded as PA, and PICAPURE HP120 8/15, coded as PP, were obtained from PICA (France); CECA CPW, coded as C was obtained from CECA (France); and Norit CGP Super, coded as NS, was obtained from Norit (the Netherlands).

2.2. Carbon synthesis

Activated carbon beads with controlled pore distributions, surface functionalisation and activation/burn-off degree were synthesised from porous phenolic resin to examine metaldehyde-carbon interactions. Phenolic carbons in this study are designated as nanoporous, nano-mesoporous and nano-macroporous. Custom-made porous phenolic resin beads were prepared following a well-established methodology where industrial Novolac pre-polymer (Hexion Specialty Chemicals Inc., UK) was cross-linked with hexamethylenetetramine (hexamine) in ethylene glycol (EG) solution dispersed in an inert mineral oil at 160 °C (Kozynchenko et al., 2002; Tennison et al., 2008; Gardziella et al., 2000). Examples of resin solution compositions used for the preparation of corresponding resin precursors are presented in Table 1. Ethylene glycol has a dual role in resin preparation: it acts as a solvent and also as a pore former. As shown in Table 1, the higher the content of the ethylene glycol in the resin solution before cross-linking, the higher the meso/macropore size and volume in the cured resin and activated carbon derivatives. After thermal curing, the beads are separated from the oil and washed with hot water (80 °C); carbonised at 800 °C in a CO₂ atmosphere and activated to prescribed burn off degrees at 900 °C.

When necessary, the surface chemistry has been modified by oxidation with ammonium persulphate in H₂SO₄ (4 N), under conditions described elsewhere (Salame and Bandosz, 1999; Wang et al., 2007; Tamai et al., 2006; Seredych and Bandosz, 2008). Sulphonic acid groups were introduced by derivatising activated phenolic carbons with sulphanic acid (Wang et al., 2007).

The introduction of amino groups was carried out by derivatising the carboxylic groups of oxidised carbons with thionyl chloride followed by reactions with ethyldiamine or N,N-dimethylethyldiamine (Tamai et al., 2006). Phenolic carbons freshly activated in carbon dioxide had a point of zero charge (PZC) of approximately 10. Carbons with PZC of 8.7 were obtained by impregnation of carbon beads with urea solution followed by calcination. Preparation details can be found elsewhere (Seredych and Bandosz, 2008). The introduction of acidic groups, described above, changed the PZC value to 2.3.

In this work, the beads denoted as TE3 and TE7 contained cross-linked resin: ethylene glycol at a proportion of 10:15 and 10:25 respectively and were nano-mesoporous carbons. The amount of carbon burn-off during the activation in CO₂ was 34% and 55%, respectively, and the particle size studied ranged from 125 to 250 μm . The beads denoted as TE8 were prepared with a proportion 10: 27 cross-linked resin: ethylene glycol respectively, with particle size of 250–500 μm and 65% burn off.

2.3. Characterisation of phenolic resin-derived beads and GAC

Pore size distribution, specific surface area (S_{BET}) and pore volume were determined via nitrogen adsorption–desorption isotherms, which were carried out on 40 mg samples at 77.4 K after outgassing at 130 °C for 24 h using an Autosorb adsorption analyser (Quantachrome Instruments, USA). A density functional theory (DFT) model was used to determine microporosity, BJH (Barrett-Joyner-Halenda) and BET (Brunauer-Emmett-Teller) models were used for pore characterisation and surface area analysis, respectively (Gregg and Sing, 1995). The total pore volume (V_p) was quantified by converting the volume of nitrogen adsorbed at $p/p_0 \approx 0.99$ (p and p_0 denote the equilibrium pressure and the saturation pressure of nitrogen at 77.4 K, respectively) to the volume of liquid nitrogen.

2.4. Adsorption experiments

Sorption was studied using batch uptake experiments detailed in the Supporting Information S1. The adsorptive capacity was calculated from the mass of metaldehyde removed from solution by the sorbent per mass of carbon, as expressed in Equation (1), where V_0 and C_0 were the initial volume of contaminated solution and concentration of contaminant, respectively, and V_t and C_t were the volume and concentration of contaminant in solution at a certain time. Adsorption studies were performed in triplicate, by incubating 20 mg of carbon in 40 ml of contaminated aqueous solution. When the aqueous solution was ultrapure water, the pH of the solution was 6.2.

$$\text{Adsorptive capacity} : (V_0C_0 - V_tC_t)/\text{sorbent mass} \quad (1)$$

Water contaminated with metaldehyde was also purified by filtration through a column packed with phenolic carbon beads. The adsorption capacity at different points of the breakthrough curve was quantified by subtracting the area below the breakthrough curve, expressed in mass of metaldehyde units, from the mass of metaldehyde filtered through

Table 1 – Solution composition for the synthesis of phenolic carbon beads with tailored porosity.

Type of porosity in the carbon beads	Resin solution composition			Meso- or macropore size, A
	Novolac, weight parts	Hexamine, weight parts	EG, weight parts	
Microporous	10	1.5	11.5	–
Micro-mesoporous	10	2	18	300–400
Micro-macroporous	10	2	30	800–1000

EG = Ethylene Glycol.

the column at a given filtrate volume. The levels of metaldehyde contamination assayed in this work, with the exception of the isotherm study, were significantly higher than environmental levels (1 µg/L), in order to compare the carbons at their maximum adsorptive capacity and also to allow observation of breakthrough using realistic volumes of spiked water (i.e. within 6000 bed volumes) during filtration studies.

2.5. Analysis of metaldehyde

Metaldehyde and d_5 -atrazine, used as an internal standard, were analysed via LC-MS as described in the [Supporting Information S2](#). The limit of detection for metaldehyde was 0.1 µg/L. Surface water samples, untreated and treated with carbon, were analysed by standard addition consisting of additional 3 non-spiked and 5 spiked levels. Before injection into the LC, sample extracts were diluted in methanol (60%) and centrifuged (10 min at 16,000 rpm) to precipitate macromolecules that could adsorb in the chromatographic column and affect the ionization in the MS ionisation source.

2.6. Statistical methods

Statistical comparison of the uptake of metaldehyde from spiked ultrapure water by phenolic carbons with different physico-chemical properties (inter-treatments/intra-water) and the application of the optimal carbon in the treatment of water from different sources spiked with metaldehyde (intra-treatment/inter-water) was performed using *one-way* ANOVA tests ($P < 0.05$). Comparison between the adsorption of metaldehyde spiked into different types of water using GAC or the optimal phenolic carbon was carried out using a *two-way* ANOVA test with replicates ($P < 0.05$).

Regression analysis was carried out to establish the correlation between the SBET of the phenolic carbons and the uptake of metaldehyde under the same experimental conditions. A two-sided *t* test was carried out to assess the correlation between the two assessed variables. Microsoft Excel software was used throughout for statistical analyses.

3. Results and discussion

3.1. Effect of degree of activation on metaldehyde adsorption

The chemical structure of the small cyclic ether which constitutes the metaldehyde molecule explains part of the difficulty associated with its removal from water. Being a polar molecule with short hydrocarbon structure implies relatively low affinity with activated carbon; previous studies report adsorptive capacities of 0.4 mg metaldehyde/g carbon for activated charcoal (Shintani et al., 1999), and up to one hundred times higher for potassium hydroxide-activated powder activated carbon (PAC) (Gessner and Hasan, 1987). PAC is not a technology that can easily be applied in wastewater treatment plants (WWTPs) due to its small particle size, and granular activated carbon is the adsorbent currently used. Since active surface is a key parameter in adsorption processes (McNaught and Wilkinson, 1997), especially in physisorption where the forces involved (van der Waals type) are not strong, the adsorption of metaldehyde should be enhanced by using carbons with higher active surface area. To test the effect of active surface area and maximise the adsorption of metaldehyde, carbons with a range of activation degrees, and hence surface areas, were synthesised and tested at equilibrium conditions. The results, expressed in various standard units, are shown in Fig. 1. As expected, increasing the degree of activation caused an increase of surface area and total pore volume, and consequently a decrease in the bulk density (Fig. 1). Notably however an increase in surface area did not increase the adsorption capacity of metaldehyde ($P > 0.05$).

Metaldehyde has an approximate area of 214.9 \AA^2 . At the working conditions of the study (40 ml of metaldehyde spiked in water at 62 mg/L, incubated with 20 mg of carbon, S1), the total number of molecules of metaldehyde in the initial solution was $8.48 \cdot 10^{18}$, which would cover a total of 18.2 m^2 of carbon surface. Each of the incubations was carried out with 20 mg of carbon, therefore, when comparing the carbons from low to high activation degree, there was 20.8 m^2 of carbon surface covered with metaldehyde, assuming a monolayer,

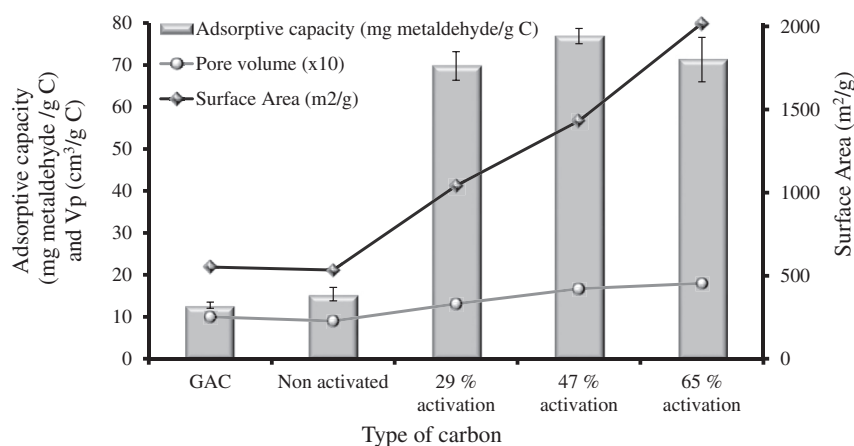


Fig. 1 – Effect of the activation degree, surface area and pore volume on the uptake of metaldehyde ($n = 3$) from ultrapure water spiked with metaldehyde (62 mg/L). Adsorption conditions are given in the Materials and Methods section and S1.

Table 2 – Removal of metaldehyde using microporous carbon expressed per units of surface, mass and volume. The range of particle sizes for the phenolic carbons M1 and M2 was 210–250 μm , and 45–125 μm , respectively. The four external carbons were PAC of size 8–15 μm . The starting concentration of metaldehyde used in contact with the carbon was 50 mg L^{-1} .

Carbon name	Structural features		Adsorptive capacity		
	S_{BET} (m^2/g)	V_p (cm^3/g)	mg metaldehyde/ $\text{m}^2 \pm s$	mg metaldehyde/g carbon $\pm s$	mg metaldehyde/ cm^3 pore volume $\pm s$
M1	1166	0.49	0.033 ± 0.002	38.4 ± 2.2	78.4 ± 6.3
M2	1188	0.51	0.034 ± 0.002	40.6 ± 2.4	79.7 ± 4.8
Picactiff EPII	1400	0.61	0.027 ± 0.001	37.6 ± 1.0	48.6 ± 1.7
Ceca cpw	1495	1.32	0.014 ± 0.001	20.7 ± 2.2	15.7 ± 1.7
Norit-CGP super	1548	1.18	0.012 ± 0.001	18.9 ± 2.5	16.0 ± 2.1
Picapure HP120 8/15	1606	1.16	0.016 ± 0.002	25.9 ± 2.5	22.3 ± 2.2

when using the carbon with S_{BET} 1041 m^2/g ; 28.6 m^2 in the carbon with S_{BET} 1432 m^2/g ; and 40.36 m^2 in the carbon with S_{BET} 2018 m^2/g . After the incubations, which were carried out until equilibria, the same amount of metaldehyde was left in solution despite the increase of active surface and the fact that these phenolic carbons were not saturated. A test for correlation showed that S_{BET} and the adsorption capacity for metaldehyde were not correlated, with $r^2 = 0.592$; t experimental and critical values for the *two-sided* t test were 1.70 and 4.30, respectively ($P < 0.05$), which supports the null hypothesis of no correlation between the two parameters. Furthermore, a negative correlation between adsorptive capacity and S_{BET} was found when the results were expressed in terms of pore volume ($r^2 = 0.9998$). Therefore, although initial activation is desirable since it removes amorphous carbon deposits from pores and therefore improves pore availability, further activation has negligible effect on the adsorption of metaldehyde. This indicates that a more complex process is governing the uptake of metaldehyde than simple surface physisorption.

3.2. Effect of pore size distribution and particle size on metaldehyde adsorption

In a scenario where a molecule does not adsorb on the carbon surface by simple physisorption, as shown above by the lack of positive correlation between the increase in S_{BET} and metaldehyde adsorption, pore-contaminant interactions may be key controls on contaminant removal. To examine the role of pore size and pore size distribution on metaldehyde adsorption, six different carbon samples where microporosity was predominant were tested for batch uptake of metaldehyde. Two microporous phenolic carbons (M1 and M2) with differences in particle size and slight differences in S_{BET} and pore volume (V_p) were synthesised by the authors and compared with the performance of four carbon samples from three different providers, described in Section 2, under batch conditions. The carbon structure was characterised via liquid nitrogen adsorption porosimetry and data are provided in Table 2 and in Supporting Information S3. The carbons studied could be separated into 2 groups based on pore size distribution; Ceca cpw, Norit CGP super and Picapure HP120 8/15 were nano/mesoporous and M1, M2 and Picatiff EPII were just nanoporous, with a narrow distribution of pores below 25 Å. Despite the differences in porosity, all the carbons tested had similar S_{BET} : $1400 \pm 186 \text{ m}^2/\text{g}$. Batch uptake results for metaldehyde (Table 2) indicate that variations in the pore size distribution influence metaldehyde uptake, with higher adsorption capacities obtained for samples with narrower pore size distribution in the micropore range. The increase of surface area did not increase the adsorption capacity, confirming earlier data.

To further examine metaldehyde adsorption processes in these carbons, kinetic studies were undertaken using high concentrations of metaldehyde (51 mg/L) (Supporting Information S1, Fig. 2). The carbons assayed had different particle sizes but similar S_{BET} , approximately 1188 m^2/g , and pore volume $V_{1.0}$ 0.51 cm^3/g , because the microporosity is the main contributor to the active surface available in this type of porous material, and the particle size represents only a relatively small contribution to it. The smallest carbon beads (<45 μm) exhibited the fastest uptake of metaldehyde and

equilibrium was reached within 10 min. For beads with intermediate particle size (45–125 μm), equilibrium was reached after 6 h, while 24 h were required for the largest beads (210–250 μm) to achieve the maximum adsorption of metaldehyde. Since surface area has been found not to influence the adsorption of metaldehyde, the more rapid uptake of metaldehyde at smaller particle sizes can be attributed to the higher accessibility (and shorter bulk transfer/diffusion pathways) of the micropores located near the particle surface. Similar results were observed under equilibrium conditions using lower concentrations of metaldehyde (0.8 mg/L), where the microporous carbons with smaller particle size (<45 μm) outperformed the larger ones (210–250 μm), with adsorptive capacities of 1.3 ± 0.1 and 1.1 ± 0.03 mg metaldehyde/g carbon respectively, difference in performance that could be attributed to differences in pore structure.

3.3. Effect of point of zero charge (PZC) on metaldehyde adsorption

The PZC indicates under which pH conditions the density charge of a surface is zero. This property can influence the attraction of substances in solution to the carbonaceous surface and variations in PZC can be achieved by controlling the atmosphere during carbon activation and the presence of oxidizing agents in solution leading to generation of carboxylic acid, hydroxyl and other groups that provide ion exchange properties (Teixidó et al., 2011; Ni et al., 2011). In the literature, carbon with surface modifications towards higher surface polarity, achieved by increasing the number of oxygen acidic groups (low PZC) have been used for the removal of metallic ions, and nitrogenated carbon (with high PZC) for the removal of species that are neutral or negatively charged at typical environmental pH such as phenol, cyanide or atrazine (for a review see Rivera-Utrilla et al., 2011).

Phenolic carbon beads, with micro and mesoporosity (TE3), covering a range of PZC have been synthesised and tested for the adsorption of metaldehyde, and performance is shown in Fig. 3. The carbons with high PZC values showed higher uptake of metaldehyde. These carbons are predominantly positively charged for a broad range of pH (via protonated carboxylic acids and basic functional groups) below the PZC. Moreover, it was found that the adsorptive capacities of the carbons with the three highest PZC, expressed in terms of pore volume, were highly correlated with PZC ($r^2 = 0.999$). Lower correlation was found when the adsorption was expressed in terms of mass of the carbon ($r^2 = 0.971$). Carbons with low PZC will stay negatively charged at environmental pH and the lower uptake of metaldehyde observed compared to high PZC values (Fig. 3) may be due to water solvation of the charged sites predominating over the interaction with metaldehyde.

3.4. Effect of surface modification on metaldehyde adsorption

The effect of PZC on metaldehyde uptake could be influenced by the nature of the functional groups providing the charge. Hence, carbon beads with different acidic and basic group functionality but similar structural features among the carbons were synthesised. The synthesis of these carbons is

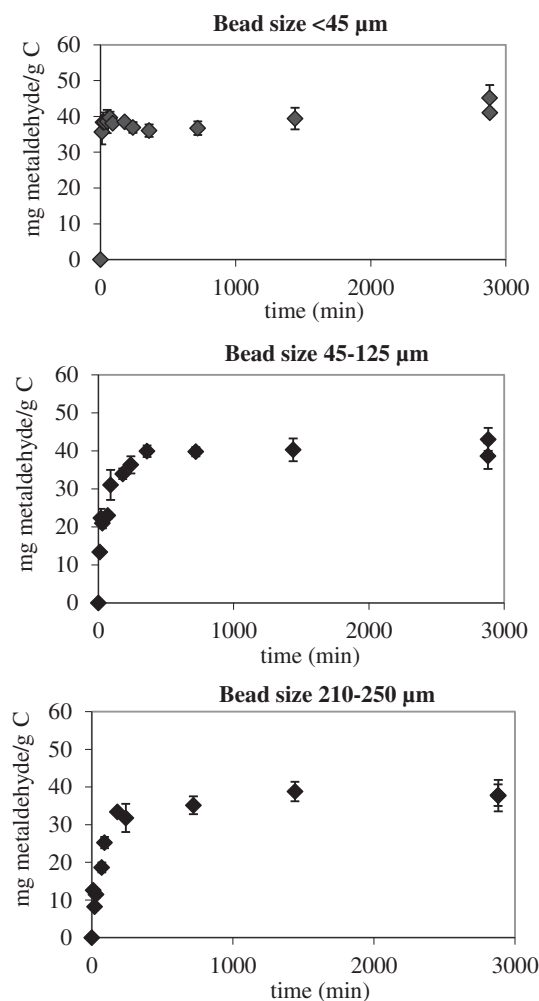


Fig. 2 – Effect of particle size on the adsorption kinetics of metaldehyde by microporous carbons, with similar SBET. Adsorption conditions are given in the Materials and Methods section and S1.

described in the Materials and Methods section. Briefly, carbon “TE3”, the starting material presented 0.58 mmol/g of combined carboxylic functions (mainly free carboxylic acid, anhydride, lactone, lactole) as determined by back titration after reaction with Na_2CO_3 ; and total acidic functionalities of 1.16 mmol/g as determined by back titration after reaction with NaOH via Boehm titration (Valente and Carrot, 2006). Hence, the phenolic OH content was 0.58 mmol/g. TE3 was oxidised to “TE3 ox”, carbon with 0.82 meq/g carboxylic acids, 0.11 meq/g carboxylic acid derivatives and 0.77 meq/g phenolic hydroxyls on the surface according to the characterisation via Boehm titration (Valente and Carrot, 2006). “TE3 ox” was derivatised with ethyldiamine “TE3-EN” and N,N dimethylethyldiamine “TE3-Me₂EN”. In addition, phenolic carbon with slightly bigger mesopores and a higher number of micropores, TE7, was modified with sulphonic acid groups at 2 different concentrations on the surface. Additional structural information on TE3 and TE7 carbons is given in the Supporting Information S4. The adsorption of metaldehyde by the range of carbons with surface modifications is shown in Fig. 4,

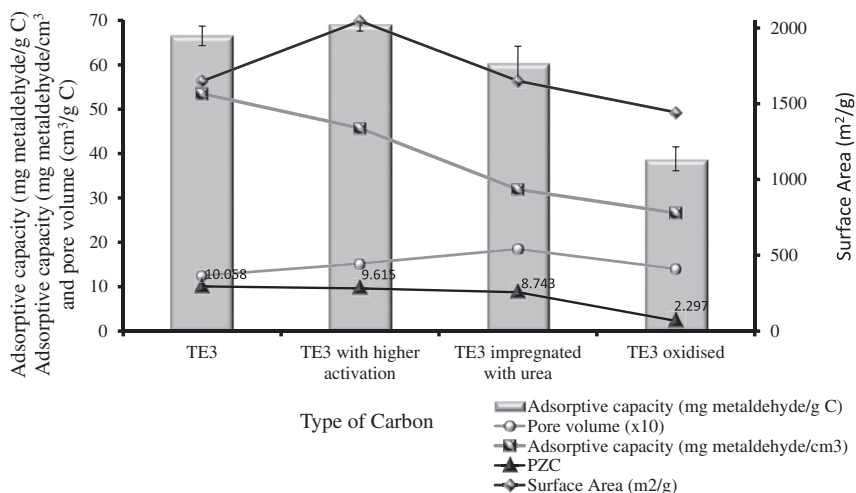


Fig. 3 – Effect of PZC on the uptake of metaldehyde, expressed in terms of sorbent mass and pore volume ($n = 6$). The starting concentration of metaldehyde was $50 \text{ mg metaldehyde} \cdot \text{L}^{-1}$. Adsorption conditions are given in the Materials and Methods section and S1.

where the uptake of metaldehyde is expressed in terms of mass of carbon and pore volume. It can be seen that surface modification leading to positive and negative surface charge caused a reduction in adsorption of metaldehyde, and the starting carbon, (carbon “TE3”), showed the highest adsorption. These results are in agreement with the data found in Section 3.3 where neutral or positively charged surfaces were found to favour the adsorption of metaldehyde. In this case, the results reveal that high positive charge density may not enhance the adsorption, possibly because metaldehyde competes with water to solvate these charged sites. The carbon sample with the highest amount of sulphonic groups and larger transport pores showed good performance, with a removal of $69.4 \pm 0.1 \text{ mg metaldehyde/g}$. This removal is probably due to the degradation of metaldehyde at the acidic sites.

3.5. Optimisation of the size of the transport pores and comparison with GAC

In general terms, the higher the amount of pore former used in the carbon synthesis, the wider the mesopores, up to macropores, and the higher the pore volume. In addition, higher activation degrees result in higher numbers of micropores, slightly broader meso and macropores and less dense carbons. Carbon beads synthesised with different amount of pore former, polyethyleneglycol in this case, and activation degree were prepared to obtain markedly different porous structure and have been assayed for the removal of metaldehyde compared to GAC. The carbon beads were TE3 (slightly mesoporous), TE7 (slightly macroporous) and TE8 (highly macroporous). The surface chemistry of both TE3, TE7 and TE8 was kept constant with 0.58 mmol/g of combined carboxylic

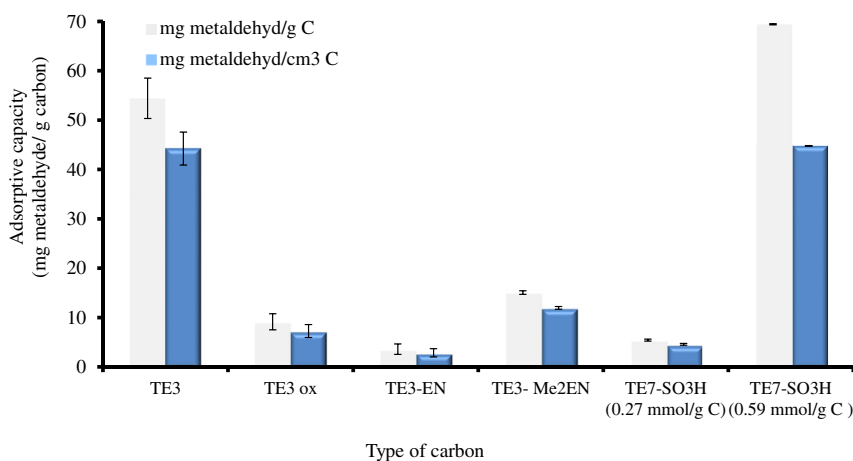


Fig. 4 – Effect of surface derivatisation on the removal of metaldehyde. Phenolic carbon (TE3), was oxidised (TE3 ox), and derivatised with ethylenediamine (TE3-EN), N,N dimethylethyldiamine “TE3-Me₂EN” and sulphonic groups “TE3-SO₃H” The initial concentration of metaldehyde was 40 mg/L . Adsorption conditions are given in the Materials and Methods section and S1.

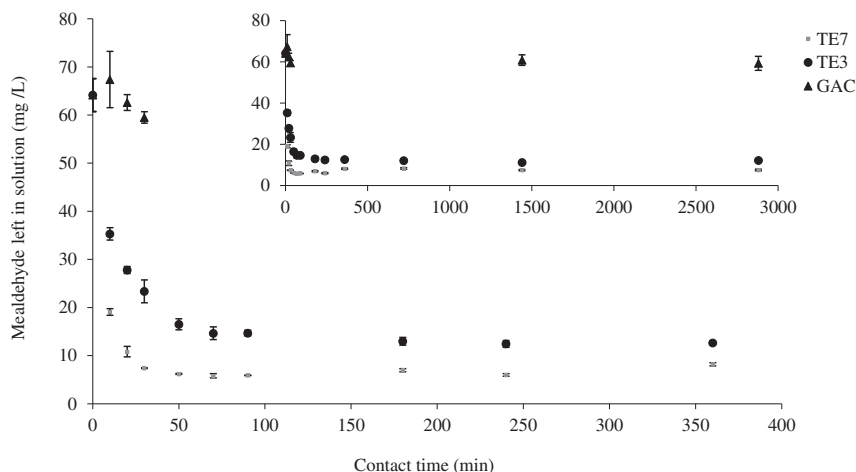


Fig. 5 – Kinetic study on the impact of transport pores on the adsorption of metaldehyde. See text for discussion of characteristics of TE7, TE3 and GAC. The error bars are hidden by the marker in some of the data points. Adsorption conditions are given in the Materials and Methods section and S1.

functions, total acidic functionalities at 1.16 mmol/g and PZC ranging between 10.022 and 10.094.

The structural characterisation of GAC via liquid nitrogen adsorption isotherms has shown an isotherm type IV, indicating dominantly microporous structure, with lower pore volume than the phenolic carbons assayed (Supporting Information S4). Pores of dimensions 11–20 Å were the main contributors to the surface area of the GAC sorbent. Mesopores were found between 21 and 38 Å and macropores were not observed.

Based on batch incubation of an aqueous solution of metaldehyde at 64 mg/L with 30 mg of each type of carbon, the removal capacity was found not to significantly differ between the phenolic resin-based carbon beads; 74.5 ± 4.23 ; 75.7 ± 1.14 ; 71.3 ± 5.34 mg metaldehyde/g carbon, for TE3, TE7 and TE8, respectively. Adsorption was much lower on GAC, at 12.8 ± 0.73 mg metaldehyde/g carbon. This indicates that slightly mesoporous carbons, achieved with the amount of pore former added to the resin indicated in Table 1 and low activation temperatures (where only 34% of carbon has been lost as CO₂ in the case of TE3), were enough to guarantee the diffusion of metaldehyde through the interconnected porous structure leading to the micropores.

The adsorptive capacity achieved with the TE3, TE7 and TE8 carbon beads almost doubled the uptake observed for beads where microporosity dominated (Table 2) at high concentrations of metaldehyde, which may indicate that transport pores, in addition to micropores, contribute to the phenomena taking place for the adsorption of metaldehyde. Fig. 5 shows the kinetics of adsorption on the optimal beads, in the size range 125–250 μm. The maximum metaldehyde uptake was reached at 30 min for TE7 and at 180 min for TE3, showing once more that transport pores, which are more abundant in TE7, are beneficial for the kinetics of adsorption.

3.5.1. Performance of optimised carbon (TE7)

A comparison between the performance of TE7, tailored for the removal of metaldehyde, and GAC has been carried out by

incubating the carbons with metaldehyde-spiked aqueous solutions until equilibria at a range of concentrations which cover realistic environmental levels (1 μg/L) to high concentrations that would only take place in the case of spillages (58 mg/L). The experimental data conform to a Langmuir model both for TE7 ($r^2 = 0.994$) and for GAC ($r^2 = 0.997$).

The Langmuir model considers the coverage of the sorbent with a monolayer of sorbate. Langmuir-type isotherms rise steeply from the origin and form a plateau with a well-marked knee, which is the case for the isotherm obtained for metaldehyde (Fig. 6). If a further rise occurred, it might have been caused by a re-orientation of the sorbate or the formation of a

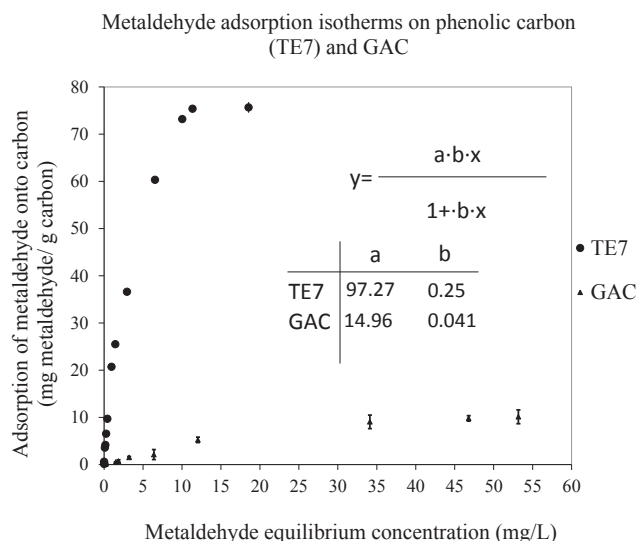


Fig. 6 – Adsorption isotherms for the removal of metaldehyde by TE7 and GAC. The parameters (a,b) show the adjustment of the experimental data to the Langmuir model. The error bars are hidden by the marker in some of the data points. Adsorption conditions are given in the Materials and Methods section and S1.

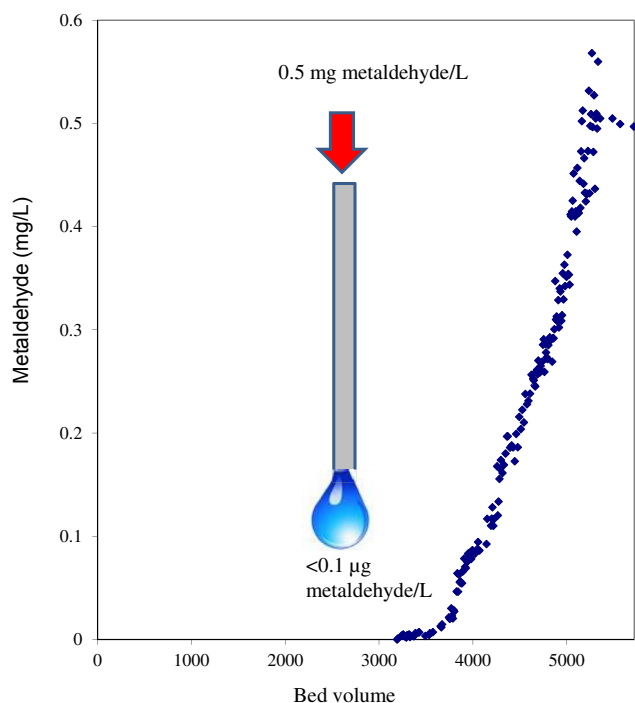


Fig. 7 – Breakthrough curve obtained when filtering ultrapure water spiked with metaldehyde at 0.5 mg/L through a column (5 mm i.d, 70 mm) packed with TE7 carbon (0.3223 g) at 0.38 ml/min and 25 °C.

second adsorbed layer, but this behaviour has not been observed here. Moreover, the slope of the curve in a Langmuir model is related to the so called “Langmuir adsorption constant” which increases with the binding energy of adsorption. Therefore, it can be distinguished that the adsorption of

metaldehyde is much stronger in the phenolic carbon than in GAC by comparing the slope of the curve obtained for TE7 and GAC.

The removal of metaldehyde was also tested in through-flow mode (Fig. 7), a mode that involves kinetic and thermodynamic components in the adsorption and is useful for upscaling purposes. The concentration of metaldehyde in the contaminated feed solution (0.5 mg/L) was selected to be higher than environmentally realistic levels by a thousand times, in order to be able to measure the breakthrough point within a week of filtration. Under the conditions specified in Fig. 7, the adsorption capacity was 6.9, 10.0 and 11.4 mg metaldehyde/g carbon at the last safe filtrate (i.e. below the 0.1 µg/L limit); at the inflexion point of the curve; and at the limit of saturation, respectively. Over 3000 bed volumes of contaminated water were treated before breakthrough. The capacity of the optimal carbon beads to remove metaldehyde was maintained in environmental (surface water) samples spiked at 5 mg metaldehyde/L, as shown in Fig. 8. The samples tested included river water (Ouse River (Sussex, UK) taken from “Spatham Lane” (freshwater tributary) and the Ouse estuary in Newhaven harbour (saline sample), water from a lake (Balcombe) and water from a reservoir (Ardingly) located in close proximity with Balcombe Lake (Sussex, UK). The performance of the carbons in these different surface water samples was also compared to tap (i.e. standard drinking) water (Brighton) and ultrapure water. This study was carried out in batch mode. Specifically, the characteristics of the waters used were: ultrapure water (pH 6.2, TOC 0.036 mg/L); tap water (pH 7.9, TOC 3.61 mg/L); Balcombe (lake) (pH 7.8, TOC 6.22 mg/L); Ardingly (drinking water reservoir) (pH 8.1, TOC 7.65 mg/L); Ouse river (Spatham lane) (pH 8.3, TOC 10.28 mg/L); and Ouse river (Newhaven) (pH 8.1, TOC 6.73 mg/L). The latter sample contained high total dissolved salts, with Na^+ 9320 mg/L; K^+ 514 mg/L; Mg^{2+} 1261 mg/L; Ca^{2+} 339 mg/L as major ions.

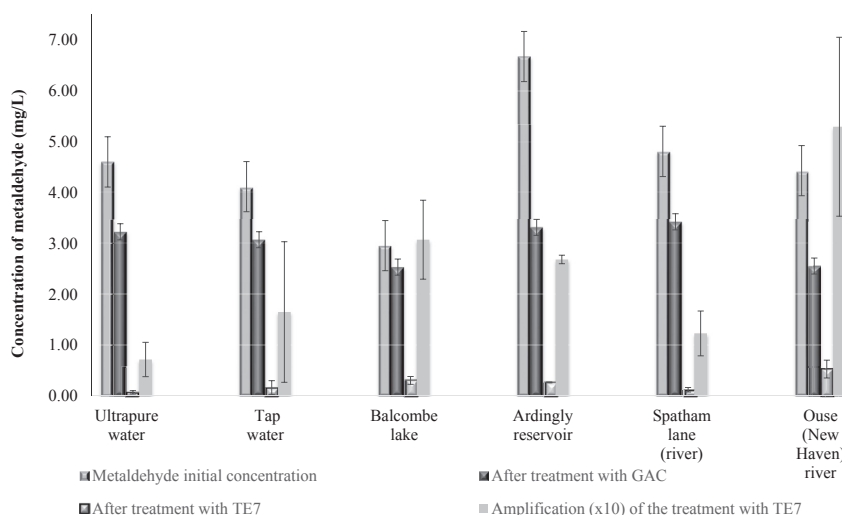


Fig. 8 – Comparison between the performance of GAC and the mesoporous phenolic carbon TE7 in the removal of spiked metaldehyde added to surface water samples from the area of East Sussex, UK. For ease of reading, metaldehyde concentrations after treatment with TE7 are also shown multiplied by 10. The error bars correspond to the standard deviation obtained from the addition standard calibration. The batch study was carried out for 48 h in an orbital shaker (at 90 rpm) at 25 °C.

Comparison between the adsorption of metaldehyde spiked into different types of environmental waters using GAC and the optimal phenolic carbon was carried out using two one-way ANOVA tests and a two-way ANOVA test with replicates ($P < 0.05$). The results from the one-way ANOVA test using GAC indicated that the performance of GAC was statistically similar for all types of water, with the exception of the sample obtained from Newhaven harbour (the sample with the highest salinity and hence a very high concentration of dissolved ions). The same test was used for TE7, and similar uptake of metaldehyde was found between the spiked water samples, with the exception of the spiked ultrapure water and water from Newhaven harbour. The two-way ANOVA revealed that the type of carbon (GAC or TE7) affected the uptake of metaldehyde significantly ($F_{\text{experimental}} = 951.561$, and $F_{\text{critical}} = 4.260$) whereas the type of water did not ($F_{\text{experimental}} = 1.629$, $F_{\text{critical}} = 2.621$). A significant interaction between the type of water and carbon used ($F_{\text{experimental}} = 5.659$, $F_{\text{critical}} = 2.620$) was found.

In all cases, phenolic carbon was shown to be highly efficient for the removal of metaldehyde, despite high levels of TOC (up to 10.28 mg/L), changes in pH (6.2–8.3) and strong differences in salinity, outperforming GAC in every case. The data indicate that the porous synthetic carbons do not “clog” or block despite high levels of organic matter in the raw surface water, nor are they highly affected by potentially competing substances from the water source. This may be an effect of the porous “skin” of the carbons, which may limit the diffusion of large molecules, and possibly the presence of selective sites which show some degree of selectivity for the adsorption of metaldehyde compared to other potential competing molecules and ions present in these waters. Indeed, the uptake of metaldehyde in these surface waters was statistically similar in all surface water samples ($P < 0.05$), with exception of the estuarine water, most likely due to the very high salinity of that water (around marine salinity). These results underline the potential for these phenolic resin-derived carbons to be used for effective metaldehyde removal in environmentally-realistic situations, as an addition or replacement to conventional GAC treatment. Based on experimental data, the “tailored” structure of these carbons (i.e. high microporosity with presence of mesopores to facilitate diffusive transport) is a significant factor in enhancing the adsorption of metaldehyde compared to conventional activated carbons. The high attrition resistance of the carbons makes them appropriate for water treatment applications although their smaller particle size compared to standard GAC implies that further adaptation of the carbons may be required to enable their use in GAC-based treatment plant. Pilot upscaling tests are currently ongoing in collaboration with the UK water industry.

4. Conclusions

- Phenolic resin-derived activated carbons with optimised structure and surface chemistry have been found to be highly effective for metaldehyde removal in environmentally-realistic situations in comparison to GAC currently used in tertiary water treatment.

- The adsorptive capacity for metaldehyde is not linked to active surface area. Adsorption is favoured in carbons with high microporosity with narrow pore size distribution, although the presence of mesopores are important in allowing effective diffusive transport of metaldehyde to active sorption sites. Surface modification of the carbon causes a reduction in adsorption capacity, due to possible competitive effects between metaldehyde and water molecules.
- Under maximum adsorption conditions, when treating water heavily contaminated with metaldehyde (64 mg metaldehyde/L) the uptake obtained was 76 mg metaldehyde/g carbon in the “designer” phenolic carbon compared with 13 mg metaldehyde/g carbon in industrial GAC. Adsorption isotherms carried out to model the adsorption of metaldehyde at a range of contamination levels, including environmentally-realistic levels, showed higher adsorption and capacity of the phenolic carbons with respect to GAC at all concentration levels.
- The adsorption of metaldehyde by the phenolic carbons, in contrast to GAC, was maintained even in the presence of high concentrations of organic matter (and inorganic salts), indicating the potential utility of these “designer” carbons in waste and/or drinking water treatment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2014.04.048>.

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