Influences on the removal of tastes and odours by PAC
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ABSTRACT

Geosmin and 2 methylisoborneol (MIB) are earthy/musty odour compounds produced as secondary metabolites by some cyanobacteria and actinomycetes. At levels as low as 5–10 ng l\(^{-1}\) in drinking water they can result in consumer complaints, and consequently their removal from potable water is a priority for many suppliers. In water treatment plants where taste and odour episodes are common, the homogenous surface diffusion model (HSDM) can be used to estimate powdered activated carbon dose requirements under a range of conditions including inlet concentration and plant flow rates (controlling PAC contact time). Water quality, in particular dissolved organic carbon concentration and character, can affect the required doses of PAC, as can the addition of chemicals such as alum and chlorine. There is significant scope for the more cost-effective utilisation of powdered activated carbon for the mitigation of taste and odours, as well as a wider range of other micro-contaminants, using tools such as the HSDM, in conjunction with knowledge of the effects of water quality and water treatment processes.

Key words | activated carbon, geosmin, MIB, tastes and odours, water treatment

INTRODUCTION

2-methylisoborneol (MIB) and geosmin are earthy/musty odour compounds produced as secondary metabolites by some cyanobacteria and actinomycetes. They can cause significant problems for drinking water suppliers as they are perceived by most consumers as an unpleasant odour and taste in water at very low concentrations (around 10 ng l\(^{-1}\)). As the compounds have an aliphatic structure not readily oxidised by the weaker oxidants such as chlorine and potassium permanganate (Lalezary et al. 1986), ozone as an oxidative treatment option has received the most attention in the literature. As with most micro-contaminants, the destruction of MIB and geosmin by ozone is strongly dependent on water quality parameters such as natural organic matter (NOM) concentration and character, alkalinity, pH and temperature (Morioka et al. 1993; Ho et al. 2002). In general, studies indicate 100% destruction by ozone cannot be expected under conditions commonly utilised in water treatment. Ozone can be used in combination with granular activated carbon (GAC); however some studies have shown that the lifetime of GAC for MIB and geosmin would be relatively short when adsorption is the predominant mechanism of removal (Gillogly et al. 1999; Ridal et al. 2001). Powdered activated carbon (PAC) can be very effective, and is often the only mode of application of activated carbon available to water authorities for the removal of taste and odour compounds. The advantages are that PAC can be applied only when required, is relatively inexpensive, and can be retrofitted to existing plants.

The major disadvantage of PAC application is that prolonged use may lead to significant costs, and this is exacerbated by the lack of knowledge regarding correct doses for the production of water of the desired quality. Dosing at levels greater than necessary can result in very high costs to the water supplier and, conversely, under-dosing leads to consumer complaints and is clearly an inefficient use of the adsorbent. Recently Cook et al. (2001) reported the application of the homogenous surface diffusion adsorption model (HSDM) for predicting activated carbon doses required at four water treatment plants supplying the city...
of Adelaide, Australia. The HSDM has been successfully applied for the prediction of the kinetics of adsorption of a range of compounds onto activated carbon (Knappe et al. 1998; Graham et al. 2000). It has also been found to be an appropriate kinetics model for the adsorption of MIB and geosmin (Gillogly et al. 1998a; Huang et al. 1996).

The model predicts the diffusion of a molecule from the external surface of the adsorbent particle, along pore surfaces, to the adsorption site. The other three mass transfer steps taking place during adsorption: transfer from bulk liquid to surface film surrounding the particle, transfer through this surface film, and the adsorption step, are not considered rate limiting in this model. The PAC particles are considered to be spherical and of homogenous structure, and Fick’s first law of diffusion is applied for the calculation of the adsorbent surface concentration as a function of the radial position within the particle. The change in bulk liquid phase concentration with time is then calculated using a mathematical model appropriate for the configuration of the system, for example, batch, plug flow or completely-stirred tank reactors (Knappe 1996). A derivation of the model and description of its use can be found in Traegner & Suidan (1989). For the application to the prediction of activated carbon doses, equilibrium and kinetic experimental results were obtained in each water and a ‘search’ computer program, utilising the HSDM, was used to determine the diffusion coefficient which best fitted the data. Other input data for this program included the PAC particle diameter and density. The diffusion coefficient was then used to predict the removal of the compounds at a range of carbon doses, contact times and initial concentrations. These predictions are specific to activated carbon and water type.

Following on from the study of Cook et al. (2001), this work highlights the factors influencing the removal of geosmin and MIB using PAC and, in particular, reports the circumstances where increased dosing may be required to achieve the desired result.

**MATERIALS AND METHODS**

**Materials**

$^{14}$C-labelled 2-methylisoborneol ($^{14}$C-MIB) was obtained from American Radio Labelled Chemicals. The solution was found to be >99% pure by GC/MS analysis. Geosmin (99.9%) was supplied by Wako Pure Chemical Industries Ltd. All other chemicals used were of analytical grade.

**Analysis**

**Geosmin**

Geosmin was analysed using solid phase microextraction—gas chromatography/mass spectrometry (SPME–GC/MS). The detection limit for geosmin using this method was 2 ng l$^{-1}$.

**MIB**

Radiolabelled MIB was analysed using a scintillation count method first reported by Gillogly et al. (1998a) and described in detail in Cook et al. (2001). This method was found to be reproducible to ± 2 ng l$^{-1}$.

**NOM analysis and characterisation**

Samples were filtered through a 0.45 µm membrane. Dissolved organic carbon (DOC) was measured using a Seivers 820 Total Organic Carbon Analyser. UV absorbance at 254 nm was obtained using a GBC UV/Vis 918 spectrophotometer. The specific UV absorbance (SUVA) was calculated using the equation: $SUVA = 100\times(abs_{254}/DOC)$. The molecular weight distributions were determined using high performance size exclusion chromatography analysis based on the method used by Chin et al. (1994). The column (Shodex Protein KW-802.5, molecular weight range 0.1 K–50 K, Waters Australia) was calibrated using polystyrene sulphonates of molecular weight 35 K, 18 K, 8 K, 4.6 K and acetone. These compounds are considered to best represent the structure and conformation of NOM in solution. Ultraviolet absorbance at 260 nm was used for detection.

**Experimental methods**

**Equilibrium isotherms**

Reservoir water was added to clean dry pyrex bottles to a level allowing minimum headspace. MIB or geosmin was
added followed by PAC. The bottle was sealed and agitated for 3–5 days. MIB and geosmin concentrations were varied between 20 and 300 ng l\(^{-1}\), activated carbon doses were varied between 2.5 and 25 mg l\(^{-1}\).

**Kinetics**

MIB or geosmin was added to a constantly stirred raw water sample. After 15 min of mixing, a sample was taken to determine the initial concentration. PAC (pre-wetted overnight) was added, with samples taken at predetermined intervals over the following 4 h. Samples were pressure filtered though 0.45 µm disposable filters to remove the PAC.

**Jar tests**

The jar test conditions replicated the conditions at the particular water treatment plant at the time the water samples were taken. Details are given in Cook _et al._ (2001).

**Chlorination**

A stock chlorine solution was prepared by dissolving chlorine gas into Milli-Q water. Water samples were chlorinated by adding an amount of chlorine water sufficient to achieve the desired dose. Reaction conditions (chlorine dose and reaction time) were set either to simulate chlorination in the distribution system relevant to the water sample, or to significantly change the nature of the NOM in the water. Chlorine concentration was determined by titration with DPD/FAS (APHA 1998).

**RESULTS AND DISCUSSION**

What PAC is best?

The most important factor influencing the removal of MIB and geosmin is the type of activated carbon used. The adsorption of MIB and geosmin has been shown to vary between activated carbons with chemically-activated wood-based carbons usually showing inferior adsorption at equilibrium (Newcombe _et al._ 1997; Chen _et al._ 1997). Pendleton _et al._ (1997), in their study of MIB adsorption onto five activated carbons, suggested this was due to the high oxygen content of wood-based carbons, producing a more hydrophilic surface and resulting in a lower adsorption energy for MIB. More recently, Newcombe (2002) showed that, for a wide range of activated carbons, the equilibrium adsorption of both MIB and geosmin can be related to the volume of micropores between 1.0 and 1.2 nm width. Adsorption isotherms of MIB onto five activated carbons are shown in Figure 1. Raw materials and activation conditions of the carbons are given in the figure. The starting concentration of MIB was 100 ng l\(^{-1}\), and the experiments were undertaken in Myponga Reservoir water, DOC = 6 mg l\(^{-1}\).

In terms of the application of PAC for the removal of MIB and geosmin, the more important factor is the removal at contact times of 2 h or less. The kinetics of adsorption of these compounds is dependent on both the equilibrium capacity of the carbon, and the volume of larger, transport pores, which allow rapid access to adsorption sites. Figure 2 shows the fraction of MIB remaining vs time, for five activated carbons. The starting concentration of MIB was 100 ng l\(^{-1}\), carbon dose was...
The variation of the fraction remaining with time will depend on the carbon dose, but is independent of the initial MIB concentration at both equilibrium, and shorter contact times. This has been shown to be applicable to micro-contaminants in the presence of NOM by a number of authors for pesticides (Knappe et al. 1998) and MIB and geosmin (Graham et al. 2000; Cook et al. 2001).

At 4 h contact time, the trend in adsorption capacity of the five carbons is: C5 > C2 > C1 > C4 > C3, the same as seen at equilibrium (Figure 1). At shorter contact times an interesting feature of the results is the unfavourable kinetics of the coconut carbons, which have relatively high equilibrium capacity, compared with the very favourable kinetics of the chemically-activated wood-based carbons, with low equilibrium capacity. These results indicate that the most efficient activated carbon for the removal of MIB in a water treatment plant will depend strongly on the contact time available for adsorption, with wood-based carbons favoured at very short contact times. These effects are readily explained by the different pore structures of the carbons. Generally, coconut carbons have a very narrow pore size distribution, possessing negligible macro- and mesopore volume (i.e. pores >2 nm width), while the wood carbons have a high volume of larger pores, or transport pores, favouring rapid diffusion to adsorption sites. Carbon C5 has a high volume of pores in the range of 1.0–1.2 nm, as well as some pores in the larger range (Newcombe et al. 2002).

Figure 3a shows the percent of MIB and geosmin removed at equilibrium for four of the five carbons. The carbon dose was 4 mg l⁻¹. Geosmin adsorbs to a greater extent than MIB, as has been noted previously (Lalezary-Craig et al. 1988). Geosmin has a slightly lower solubility than MIB, and is flatter in structure, both of which can be expected to have an influence on the adsorption. Apart from the difference in the overall adsorption, the trend for the activated carbons is the same for the two compounds.

In contrast, at 60 min the trends are different for the two compounds (Figure 3b). For geosmin, the two wood-based chemically-activated carbons, C3 and C4, are far superior to the other carbons at 60 min contact time, whereas for MIB the differences are smaller. This indicates that the advantage to the kinetics of adsorption provided by the transport pores of the chemically-activated wood carbons was more pronounced for geosmin. This supports the finding by Cook et al. (2001) that the kinetics of adsorption of geosmin were slower than MIB on a coconut carbon, with diffusion coefficients for MIB in four reservoir waters an order of magnitude higher than those for geosmin. This result also suggests that chemically activated wood carbons containing a large volume of transport pores may be the carbons of choice for geosmin,
whereas for MIB the best carbon will be dependent on the contact time available.

It should be noted that desorption of MIB from chemically-activated wood carbons has been reported (Newcombe & Drikas 1994; Hepplewhite 2000; Newcombe et al. In press) and may affect treated water quality, depending on the residence time of sludge in sedimentation basins. Desorption of geosmin has not been investigated.

PAC particle size also plays an important role in the kinetics of adsorption of MIB and geosmin. A smaller particle size results in shorter distances for the compound to travel before reaching adsorption sites, and a higher external surface area for the adsorbate to access the internal pore structure of the carbon, and consequently improved kinetics would be expected. For example, Figure 4 illustrates the difference in the doses required for the reduction of geosmin concentration by 50% in 60 min for a range of influent concentrations for the two particle sizes. The doses were calculated using the HSDM as described in the introduction.

Clearly there is a particle size limit below which ease of handling of the PAC becomes an issue. A very small particle size may also result in removal difficulties using conventional methods, and possible breakthrough into the distribution system. The 10 µm median particle size has proven to be optimum for the water treatment plants supplying Adelaide, using both conventional and dissolved air flotation technology.

**PAC dose predictions**

Once the most appropriate activated carbon has been chosen for the water treatment plant conditions, the determination of appropriate dosing criteria is the most important aspect of PAC application. The application of the correct dose for achieving the desired water quality is the aim of the water treatment operator.

The homogenous surface diffusion computer model (HSDM) has been applied to PAC adsorption in inlet waters to four water treatment plants around Adelaide, and has been shown, under most circumstances, to predict the level of removal of geosmin and MIB obtained in laboratory jar tests (Cook et al. 2001). The conditions under which the model is less successful are described in the following sections. Figure 5 shows experimental data for the removal of MIB at three activated carbon doses (activated carbon C2) in Hope Valley Reservoir water (DOC = 5 mg l\(^{-1}\)). Curve (a) data were used to determine the parameters required for the application of the model, along with equilibrium adsorption data (not shown). Those parameters were applied to predict the removals at
two other carbon doses (curves (b) and (c)). The figures show that the predictions were excellent. Similar experiments were undertaken in inlet water from the other three plants, and from this information, PAC dosing tables were constructed for the water treatment plants. These tables are now used for the determination of PAC application rates. Investigation of historical data showed that the predictions can be directly related to the actual removals of geosmin, with an $R^2$ value of 0.74, indicating that the application of the dose tables should result in correct PAC dosing regimes (Cook et al. 2000).

**Influence of raw water quality on PAC doses for MIB and geosmin removal**

Once the appropriate PAC doses have been determined for a particular water source, the question to be answered is ‘How will changes in raw water quality affect PAC doses?’

**Alkalinity, pH, ionic strength**

Alkalinity, ionic strength and pH do not appear to affect the adsorption of MIB and geosmin over the ranges generally encountered in drinking water treatment. Extreme pH adjustment results in a decrease in adsorption at pH 4 and below. Although Graham et al. (2000) suggested this effect was due to enhanced competition with NOM at lower pH, the effect was also seen in the absence of competing substances (Newcombe, unpublished data). The cause of this reduced adsorption is not known, however it will not be encountered under normal plant operating conditions.

**Dissolved organic carbon concentration and character**

Dissolved organic carbon (DOC) concentration and character have both been reported to strongly affect the adsorption of MIB (Newcombe et al. 1997; Cook et al. 2001; Newcombe et al. In press). Figure 6 shows how seasonal changes in water quality can affect the equilibrium adsorption of MIB. Five water samples were taken from Happy Valley Reservoir at various times during the period 1998–1999. One sample, W4, was also diluted by a factor of two (W4 diluted). Three samples were taken from Hope Valley during this period, and one each from Myponga Reservoir and the inlet to Anstey Hill water treatment plant (prechlorinated River Murray water). Adsorption of geosmin at equilibrium is not affected significantly by water quality changes (Cook et al. 2001). As MIB adsorption is not influenced by changes in alkalinity or pH, differences in the equilibrium adsorption curves shown in Figure 6 are attributable to variations in NOM character and concentration.

Table 1 shows the DOC concentration, UV absorbance at 254 nm, SUVA and the PAC dose required to reduce the MIB concentration by 50% in 1 h in each water.

UV absorbance, SUVA and DOC concentration were plotted against the PAC doses given in Table 1 in an effort to determine a relationship which could be used in practice. Figure 7 shows that there is no significant relationship between carbon dose and these parameters.

The lack of any significant relationship is a result of the nature of the competitive effect. The majority of the effect is due to direct competition for adsorption sites between MIB and small, uncharged NOM compounds with low UV absorbance (Hepplewhite 2000; Newcombe et al. In press). The concentration of competitive NOM in Myponga water was estimated using the equivalent background compound model (EBC). This can be used to
obtain the adsorption isotherm of competing compounds when the adsorption of the target compound is known in the presence and absence of the NOM (Najm et al. 1991; Knappe et al. 1998). The EBC is not considered to be the entire NOM present in natural waters, as only an unknown portion of the NOM will compete. The model uses ideal adsorbed solution theory (IAST) to obtain the EBC adsorption parameters (Freundlich K, 1/n and initial EBC concentration) by the minimisation of the error between the experimental adsorption isotherm in the presence of NOM and the adsorption isotherm predicted by the IAST model. More detail on this procedure is given in Najm et al. (1991) and Newcombe et al. (In press). In the latter study the concentration of the EBC, or the competing NOM, was found to be less than 10% of the total NOM. Therefore bulk characterisation and concentration parameters would not be considered specific enough to give an indication of the extent of competition to be expected in a particular water. A technique sophisticated enough to discriminate the compounds responsible for the reduction in adsorption capacity, such as molecular weight distribution using DOC detection, are out of the reach of water treatment operators. To date, the best predictor of an increased PAC requirement is an increase in the DOC, although this cannot be considered an accurate predictor (Figure 7).

Influence of water treatment processes on PAC doses for MIB and geosmin removal

Chlorination

Several studies have shown that the inlet water to one Adelaide water treatment plant, Anstey Hill, contains organic compounds which are more capable of effectively competing with MIB for adsorption sites than NOM in other waters (see Figure 6). The adsorption of MIB was consistently lower in this water than others of higher DOC (Cook et al. 2001; Newcombe et al. 1996). The inlet water to Anstey Hill was generally pre-chlorinated, as the water treatment plant is at the terminal of a 60 km pipeline from the River Murray, and several off-takes along the pipe supply households with potable water. Figure 8a shows...
the removal of MIB with time in four water samples: (i) raw River Murray water, (ii) Anstey Hill inlet water in the absence of chlorination, (iii) water sampled at Mannum, 2 km downstream from the chlorination point in the pipeline, and (iv) Anstey Hill inlet water where pre-chlorination was applied at the river off-take. No free chlorine was present during these experiments, as the presence of chlorine has also been shown to reduce the adsorption of MIB and geosmin (Gillogly et al. 1998b; Lalezary-Craig et al. 1988). Clearly the pre-chlorination of the water has a significant effect on the adsorption of MIB, and the effect occurs early in the pipeline, presumably immediately at chlorination. A simulation of the chlorination of the river water was undertaken in the laboratory, with the same significant decrease in MIB adsorption (Figure 8b). The effect can be interpreted as the increase in adsorption competition provided by the chlorination by-products, generally smaller molecules, more likely to provide direct competition with the target compound.

This effect has been seen, to a less significant extent, with the laboratory chlorination of a range of NOM isolates from Hope Valley Reservoir (Caire 1998). However the same effect was not seen in a Lake Michigan water in the USA (Gillogly et al. 1998b) or Myponga Reservoir water (Figure 9). DOC, SUVA and UV absorbances of the waters used in Figures 8 and 9 are given in Table 2. Figure 10 shows the effect of chlorination on the molecular weight distributions of River Murray and Myponga Reservoir water. It is clear that the chlorination process has a significant effect on the character of the NOM. In the case of the extreme conditions in the Myponga water (30 mg l\(^{-1}\) applied chlorine), a large increase in smaller molecular weight NOM is seen. This increase in smaller NOM on chlorination has been reported previously for NOM fractions (Pelekani et al. 1998). Once again, none of the characterisation techniques used can aid in the interpretation of the competitive effects with MIB. The main difference apparent between the two waters is that the river NOM

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**Figure 8** | MIB removal as a function of time in chlorinated and non-chlorinated River Murray water.

**Figure 9** | MIB removal as a function of time in chlorinated and unchlorinated Myponga Reservoir water. Residual chlorine was quenched prior to experiment.
appears to be more susceptible to attack by the chlorine as at 5 mg l\(^{-1}\) chlorine dose the SUVA was reduced to 1.5, whereas, even at a 30 mg l\(^{-1}\) chlorine dose, the SUVA was only reduced to 2.7 in Myponga water (Table 2). Furthermore, a doubling of the chlorine dose from 15 to 30 mg l\(^{-1}\) resulted in no further degradation of the SUVA in Myponga water, indicating that the possible reactions had already gone to completion at the lower dose. This aspect of prechlorination requires further investigation, although it appears to date that the effects of chlorination of the River Murray NOM may be specific to this source.

**Coagulation/flocculation**

It has been reported that the application of PAC at the point of addition of alum or other coagulants reduces the adsorption efficiency (Najm *et al.* 1991). In their study of a range of waters, Cook *et al.* (2001) found that the efficiency of the activated carbon was only reduced under conditions of high turbidity, and therefore high alum doses. The adsorption of MIB and geosmin are not affected by the presence of high turbidity levels (unpublished data). However, in a jar test where the PAC was added during alum flocculation, the turbidity of the water had a significant effect on the removal of geosmin (Figure 11a). The same effect was noted for MIB. The HSDM model was used to predict the removal in the absence of coagulation, and the predicted removals are also shown in Figure 11a. In three other waters with turbidities below 26 NTU, no such effect was noted, and the HSDM predicted the removal accurately.

This reduction of removal efficiency is attributed to the binding of the PAC in the floc. The effective contact between the water and the PAC will depend on the size...
and density of the resultant floc; for example, more efficient contact could be expected from a small floc with loosely bound particles, than a large dense floc. Figure 11b shows that DOC concentration also has an effect on the removal efficiency when PAC is added during coagulation. In this case Happy Valley Reservoir water was diluted to obtain a lower DOC, then additional turbidity was added, obtained from a 0.2 µm filtration of river water, to obtain the same high turbidity. Therefore, the water represented the same turbidity and NOM character as the original reservoir water, but a lower DOC concentration. The results suggest that a decrease in the DOC while the turbidity and alum dose remain constant, may produce a floc that results in a lower effective contact between the PAC and the MIB/geosmin.

CONCLUSIONS AND RECOMMENDATIONS

The first consideration for water suppliers using activated carbon to deal with taste and odour episodes caused by MIB and/or geosmin is choosing the most effective adsorbent. In general, good quality microporous carbons, such as coconut or coal-based carbons, will be superior, although at shorter available contact times the chemically-activated wood carbons may provide better adsorption kinetics.

In water treatment plants where taste and odour episodes are common, the homogenous surface diffusion model (HSDM) can be used to estimate powdered activated carbon dose requirements under a range of conditions including inlet concentration and plant flow rates (controlling PAC contact time). This information allows water suppliers to make informed decisions regarding treatment options, and in most cases a good quality PAC may be sufficient for the mitigation of the problem. In cases of prolonged episodes, and high inlet levels, an estimate of the carbon doses required, and knowledge of the common time frame over which the taste and odour compounds will be present, will allow a cost-benefit analysis of PAC application vs more advanced treatment processes. This is information that most water authorities currently do not have.

When PAC is the desired option, the HSDM predictions can be routinely used for estimates of the required doses when the operators have knowledge of approximate inlet concentrations and available contact times. Such information will soon be utilised at four water treatment plants in Adelaide, Australia, in the form of a ‘user-friendly’ computer program. However, the PAC dose predictions must be used in combination with knowledge of the effect that water quality changes and water treatment chemicals have on the removal of MIB/geosmin.
In general, an increase in DOC, often reflected in an increase of UV absorbance, a parameter more routinely analysed, will result in an increased carbon dose requirement for MIB removal. Geosmin is less sensitive to changes in DOC quantity and quality, and no adjustment in the dose may be required. For example, in Adelaide the major compound of concern is geosmin, and PAC dose predictions have been validated under conditions of a 100% increase in DOC concentration. Pre-chlorination is not recommended in situations where PAC is used for taste and odour mitigation. Evidence is clear that a chlorine residual can reduce the adsorption of MIB and geosmin and, in at least one case, the effect on NOM can lead to increased adsorption competition, and reduced MIB adsorption. Again, geosmin is not affected by the variation in NOM character brought about by chlorination.

The application of PAC simultaneously with alum or other coagulants, a common practice, can result in a decrease in the removal of both MIB and geosmin, and therefore an increased dose requirement. The magnitude of the effect will depend on the size and structure of the floc formed containing the PAC particles, which in turn is dependent on alum dose, turbidity, DOC concentration, and colour, if this is one of the criteria for alum dosing. In general terms, a higher alum dose, driven by an increase in turbidity, will probably lead to a higher PAC dose requirement than predicted by the HSDM.

In summary, there is significant scope for the more cost-effective utilisation of powdered activated carbon for the mitigation of taste and odours, as well as a wider range of other micro-contaminants, using tools such as the homogenous surface diffusion model, in conjunction with knowledge of the effects of water quality and water treatment processes.

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