Adsorption of MIB by activated carbons produced using several activation techniques

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Abstract Water treatment authorities use activated carbon as the best available technology to remove low molecular weight organic compounds from potable water. In Australia, pollutants of concern include secondary metabolites from bacterial and cyanobacterial blooms which are highly odorous and, in some cases, toxic. Of these compounds, 2-methylisoborneol (MIB) is one of the most common and its unpleasant musty earthy odour can be detected at or above approximately 10 ng/L. Difficulties in using activated carbon to target such small organic compounds arise when the water has high concentrations of natural organic matter (NOM), as these compounds also adsorb on activated carbon. The adsorption of NOM on activated carbon increases the cost of using this material in water treatment due to competition with the target organic compounds, reducing the capacity of the activated carbon for the latter. The surface of activated carbon can be tailored during production to provide physical and chemical characteristics that can either aid or hinder the adsorption of particular compounds. One source of activated carbon currently under investigation at RMIT University is brown coal char waste from power stations. This waste, currently disposed of to landfill, is potentially an option for activated carbon production. This material has the advantage that it has already been carbonised at around 500°C in the power generation process. This means that less energy is required to produce activated carbon from power station char compared to coal, making the final product cheaper to produce. Previous work at RMIT has shown that steam activated power station char can remove organic compounds from water. Production of a range of activated carbons from power station char (PSC) was undertaken using different activation methods, including steam activation, steam activation with acid pre-treatment, alkali heat treatment, and Lewis acid heat treatment. The different activation methods produced activated carbons with different pore size distributions, in particular, the acid pre-treatment increased the surface area and porosity significantly compared with steam activation, and the alkali treatment increased the microporosity. Adsorption of MIB on these activated carbons was evaluated to determine the relationship between physical and chemical interactions of the activated carbon and adsorption. Adsorption of MIB on these activated carbons was found to be dependent on the secondary micropore volume. Lewis acid treatment and alkali treatment was not involved in the generation of many of these secondary pores, hence carbons from these treatments did not perform well in adsorption tests. The best adsorption results were achieved with steam activated or acid treated steam activated samples which performed comparably to commercial products. Initial results showed that competition from NOM adsorption was lowest with the PSC activated carbons, allowing greater adsorption of MIB, compared with the commercial activated carbons.

Keywords 2-methylisoborneol; activated carbon; brown coal

Introduction

Production of a high quality water supply from low standard inlet water can be expensive, thus there is a need for improved efficiency and reduced costs in water service provision and treatment. The production of high quality potable water from low quality raw water may require the removal of many unpleasant taste and odour compounds. In particular, surface water supplies are prone to algal or bacterial outbreaks which produce secondary metabolites such as 2-methylisoborneol (MIB) and geosmin which are noticeable at low concentrations (ng/L). Adsorption on activated carbon is used in water treatment as the best

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available technology to remove these target organic compounds (US EPA Office of Drinking Water, 1990).

Large amounts of activated carbon are often used in water treatment and it is desirable to increase the efficiency of the adsorption process to reduce the amount of adsorbent required, and hence reduce costs. A significant reduction in the adsorption of low molecular weight organic compounds arises when the water has a high concentration of natural organic matter (NOM) as NOM can also adsorb on activated carbon. The higher concentrations (mg/L) of NOM compete for adsorption sites, reducing the capacity of the activated carbon for the target compounds.

Work by Othman (1999) showed that activated carbon produced from waste char from a Victorian power station (PSC) was comparable to commercial products for the removal of 4-nitrophenol from water. As the PSC starting material is a char, less energy is required during activation than for raw coal, making the final product potentially cheaper to produce than current commercial carbons. Different activation methods have been found to influence the adsorption properties of activated carbons. Activated adsorbents from brown coal have been found to possess increased hardness and surface area/microporosity when activated using potassium hydroxide (KOH) (Durie and Schafer, 1979; Guy and Perry, 1992) or zinc chloride ($ZnCl_2$) (Usmani et al., 1996). Varied success in increasing the adsorbent porosity was found when the brown coal was acid leached prior to activation. These chemical treatments change the surface chemistry of the activated carbon (particularly the oxygen content). These changed surface properties may influence the adsorption process, e.g. hinder the adsorption of MIB (Pendleton et al., 1997). The different chemical activation methods also generate different pore size distributions within the activated char. Porosity appears the most important parameter for MIB adsorption, with the secondary micropore volume (pore diameter approximately 0.7–2.0 nm) suggested as the most influential factor on MIB adsorption (Newcombe, 2000).

In this study, activated carbon produced from PSC was manufactured using four different activation methods: steam, KOH, $ZnCl_2$, and acid leaching. The resultant products were then assessed with respect to MIB adsorption.

Experimental conditions

Activated chars were produced from a de-ashed product from the Yallourn power station in Victoria (PSC) (HRL Technologies, Victoria). The acid-treated char was soaked overnight with concentrated HCl, then rinsed thoroughly and dried before steam activation. The KOH-treated char was soaked overnight (coal:KOH ratio of 1:0.5) and dried before activation in the presence or absence of steam. The $ZnCl_2$-treated char was soaked overnight with a coal:$ZnCl_2$ ratio of 1:2. All chars were activated at a temperature of 900°C, with the exception of the $ZnCl_2$-treated char which was activated at 650°C. The coal-based activated carbon Filtrasorb 400 (F400) (Calgon Carbon) was used as a representative commercial adsorbent. All samples were washed and ground to a particle size of <53 μm. Surface area and pore size distribution analysis was performed using nitrogen gas adsorption (Micromeritics ASAP 2000 instrument). Samples of adsorbent were heated to 250°C until completely outgassed (approximately 6 hours, or overnight).

XPS analysis of the adsorbent samples was carried out using a MicroLab 310-F (Fisons Instruments, Hastings, UK) instrument with a non-monochromated Al Kα source of 1486.6 eV. The high resolution scans were conducted using a pass energy (constant analyser energy mode) of 10 eV over the binding energy range, 280–295 eV for carbon (5 scans, 50 meV step), and 525–545 eV for oxygen (10 scans, 50 meV step).

Equilibrium isotherms of ^{14}C-MIB (150 ng/L) were determined using a carbon dose range 2–20 mg/L and a background concentration of 0.01 M NaCl (or 0.01 M NaCl and

10 mg/L NOM when determining competitive isotherms). Samples were mixed for three days, then analysed using 2.5 mL filtered sample and 17.5 mL of scintillation cocktail (Starcint, Canberra Packard) in 20 mL scintillation vials, shaken vigorously. After standing for a minimum of 1 hour the vials were counted once for 20 minutes (2σ value of 0.5, where σ is the standard deviation) on a Tricarb 2500TR (Canberra Packard) liquid scintillation counter.

Results and discussion

The pore size distribution of the five activated carbons varied significantly, depending on the different activation techniques. The micropore distributions for the activated chars produced in this study appear to be grouped, depending on the activation treatment (Figure 1a). The $ZnCl_2$ and steam only activated chars possessed the lowest total micropore volumes and similar distributions. These micropore values were much lower than for the other activated chars, although there was a substantial increase in micropore volume compared with that of the PSC. The acid treated activated carbon had the highest micropore volume, and a wide distribution of micropores. Both activated chars treated with KOH had high micropore volumes and the presence of steam during activation did not appear to affect micropore development substantially. However as shown in Figure 1b, the mesopore volume of the KOH-activated chars can be increased by the addition of steam. As MIB is a small molecule (diameter approximately 0.6–0.7 nm), the micropore region of an adsorbent is important in determining its adsorption capacity for this molecule.

The mesopore distributions (Figure 1b) show that a broad range of values can be produced. The steam activated carbon, S-AC, had the highest total mesopore volume and a broad range of pore sizes, including a large volume of pores at the larger end of this range. The acid leached char, HCl-AC, had a much lower mesopore volume and almost all pores present had a diameter of <10 nm. The steam activated KOH char, SKOH-AC, had a very similar mesopore distribution to HCl-AC, with slightly more pores present with diameter of <5 nm. The KOH activated char, KOH-AC, had a much lower mesopore volume than SKOH-AC, showing the effect of the presence of steam during the KOH activation of the char at the same temperature. The zinc chloride activated char, $ZnCl_2$-AC, had a very low mesopore volume and pore size distribution, lower than that of the PSC feedstock. This
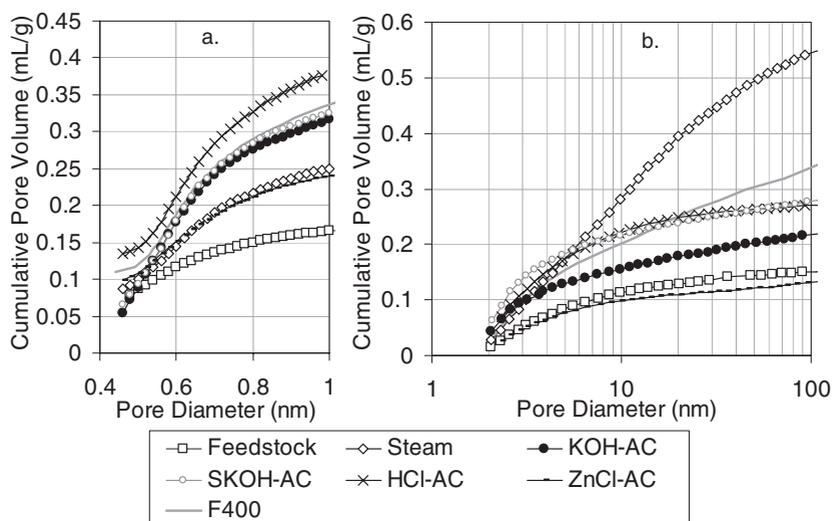
Figure 1 (a) The micropore distribution; and (b) the mesopore distribution for five activated chars, the feedstock PSC and F400

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suggests that the $ZnCl_2$ treatment conditions chosen were too mild for activation of a charred material, compared with the activation of a brown coal, and that there may have been some pore blockages caused by the $ZnCl_2$.

The different activation treatments also changed the functional groups present on the surface. From XPS results the HCl pre-treatment reduced the amount of oxygen present on the surface, whereas the KOH treatment increased the amount of oxygen on the surface (Table 1). S-OH and $ZnCl_2$-AC had lower amounts of oxygen present on the surface than PSC, indicating a removal of some oxygen during activation. However, this is based on the assumption that these values were representative of the surface of the internal pores. When produced from the same feedstock, it was shown that the presence of oxygen functional groups on the surface of activated carbon can play a role detrimental role in MIB uptake (Pendleton *et al*., 1997).

Comparison of adsorption of MIB by the new carbons and the commercial activated carbon, F400, was undertaken. F400 is a coal-based activated carbon that has a high adsorption capacity for MIB, and has a higher uptake than the trial adsorbents (Figure 2). Of the activated chars, HCl-AC had the highest uptake, which was expected since it had the highest micropore volume. SKOH-AC had a higher MIB removal than KOH-AC, yet these activated chars had similar micropore distributions. This suggests that the mesopores (the volume of which is substantially higher for SKOH-AC) may play a role in the adsorption of MIB. However, the steam only activated adsorbent, S-AC, had similar MIB removal levels to the $ZnCl_2$-AC, which suggests that the mesoporosity difference for these two activated chars was less important. This may be because the S-AC had a large volume of larger mesopores, unlike SKOH-AC where the mesoporosity was generated predominantly by the smaller pores in this range.

The secondary micropore volume may be the most important parameter for determining the adsorption of MIB, as pores in this range are likely to exhibit enhanced adsorption of MIB (since all pore walls are involved in the adsorbate/adsorbent interaction). The adsorption of MIB by the five new adsorbents was shown to be highly dependent on the secondary

Table 1 O/C ratios for the five activated chars and PSC

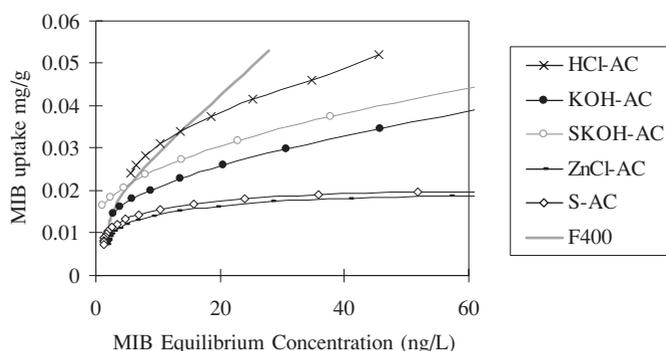| Sample	Activation method	O/C ratio
PSC	None	0.23
S-OH	Steam	0.19
HCl-AC	HCl + steam	0.06
KOH-AC	KOH	0.38
SKOH-AC	KOH + steam	0.33
$ZnCl_2$-AC	$ZnCl_2$	0.17

Figure 2 MIB isotherms for the five new activated chars compared to F400, a commercial activated carbon

micropore volume, where the secondary micropore volume has a linear relationship with the Freundlich constant (K_f) for the activated chars (Figure 3).

These adsorption data were compared with those for F400, which had a similar secondary micropore volume to HCl-AC (Figure 3). In a single solute environment the activated carbons had a much lower uptake of MIB than expected compared with F400. This suggests that within a series of activated carbons produced from the same source, a linear relationship between secondary micropores and the MIB uptake occurs; however, this relationship may fail when comparing carbons produced from different sources.

It is difficult to determine the reason for the difference in adsorption of MIB between F400 and the activated carbons. The dependence of the MIB uptake on the secondary micropore volume suggests that the chemical treatments used have little effect on MIB adsorption. Similarly, Herzing *et al.* (1977) showed MIB adsorption was unaffected by the difference in pH caused from different chemical treatments. Another possible cause for the reduced uptake is the presence of oxygen, however the new adsorbents show a large range of O/C ratios (the KOH chars have a high O/C ratio, the steam activated chars a low O/C ratio, Table 1). If adsorption were dependent on this factor, it is unlikely that the uptake of MIB would show a linear trend with the secondary micropore volume for these adsorbents. The cause of the unexpectedly low uptake of MIB on the new activated chars has yet to be explained.

As HCl-AC had the highest MIB uptake under these conditions, adsorption of MIB in the presence of NOM was investigated for this adsorbent. HCl-AC had a higher uptake of MIB than F400 (Figure 4) despite the similarity of secondary micropore volume for the two adsorbents. Other work by the authors (McCallum, 2001) suggested a weak interaction between NOM and the adsorbent surface of HCl-AC. Thus the MIB may adsorb preferentially as the energy of adsorption is more favourable than for NOM adsorption. As MIB adsorption is not affected by the presence of surface functional groups to the same extent as NOM, it is possible that the surfaces of the PSC-derived activated chars have different surface functional groups compared with the commercial carbon, which affect the adsorption of NOM.

Conclusions

Activated carbons with a range of pore size characteristics can be produced from PSC. The HCl pre-treatment appeared the most effective for increasing the micropore volume. Treatment with KOH in combination with steam appeared the most effective way of controlling the microporosity/mesoporosity, as in the absence of steam a highly microporous carbon is formed. As steam is added, the mesoporosity is increased. Zinc chloride was the
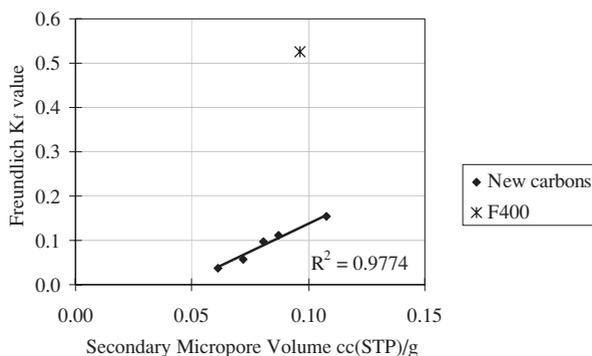

Figure 3 The relationship between the secondary micropore volume and the MIB uptake on the new adsorbents and F400
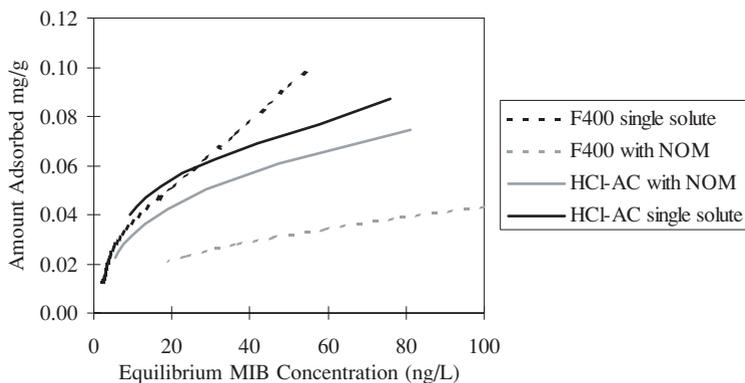
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Figure 4 Uptake of MIB in a single solute environment, and in the presence of 10 mg/L NOM, by the commercial activated carbon F400 and the trial activated carbon HCl-AC

least effective treatment as the temperature used for activation with this additive was too low to substantially increase the porosity of the PSC.

Adsorption of MIB for this series of adsorbents appeared to be dependent on the secondary micropore volume and independent of the surface oxygen content. The adsorption of MIB was low compared to the commercial activated carbon (F400). However, in the presence of NOM, the HCl-treated activated carbon had a higher uptake of MIB than the commercial activated carbon, suggesting that pore size distribution is not necessarily the most important characteristic for adsorption under these circumstances.

Acknowledgement

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