

# Adsorption of 2-methylisoborneol and geosmin by a low-cost hybrid adsorbent synthesized from fly ash and bentonite

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## ABSTRACT

This paper describes the synthesis of a low-cost hybrid adsorbent from activation of fly ash and bentonite to remove 2-methylisoborneol (MIB) and geosmin from water. These substances produce objectionable taste and odor problems at levels as low as 4–10 ng/L and an effective, low-cost method of removal would be useful. The effect of the initial pH, contact time and adsorbent dosage on the adsorption process was investigated. In the range of 42–234 ng/L of MIB and geosmin, the maximal adsorption efficiency was obtained at the conditions of a dose level of 15 mg/L adsorbent, pH 8 and 60 min contact time, reaching 59.9 and 63.7%, respectively. Comparing to the natural fly ash and bentonite, the adsorbent showed higher surface area and micropores. The interlayer distance of the hybrid adsorbent was 0.59 nm, in accord with the molecular dimension of MIB and geosmin. The effect of humic acid, representative of natural organic matter (NOM), on MIB and geosmin adsorption was investigated for adsorbent systems and indicated the presence of NOM would decrease adsorption slightly. The leaching experiments showed that the leaching of heavy metals from the adsorbent was negligible.

**Key words** | adsorption, bentonite, fly ash, geosmin, 2-methylisoborneol

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## INTRODUCTION

Taste and odor (T&O) are a major quality concern of drinking water. Earthy–musty odors originate from microbial metabolic by-products, such as 2-methylisoborneol (MIB), geosmin, isopropyl methoxypyrazine (IPMP) and MIB and geosmin have been identified as a major cause (Bruce *et al.* 2002). MIB and geosmin can be sensed at levels as low as 4–10 ng/L (Suffet *et al.* 1999). Therefore, an efficient, economic treatment method for these compounds is highly desirable for producing high quality potable water (Pirbazari *et al.* 1993; McGuire 1995). The presence of high concentrations of natural organic matter (NOM), a complex mixture of organic compounds derived primarily from the decay of plant and animal materials, may adversely affect the adsorption capability of adsorbent (Chestnutt *et al.* 2007).

It has been reported that conventional water treatment processes, such as coagulation, sedimentation and filtration, do not efficiently remove MIB and geosmin (Anselme *et al.* 1988; Bruce *et al.* 2002). Special treatments such as oxidation are necessary for satisfactory removal (Glaze *et al.* 1990). The oxidation process requires expensive chemicals and often produces objectionable by-products (Cook *et al.* 2001). The current practice most commonly followed is the application of activated carbon treatment during severe taste and odor outbreaks (Cook *et al.* 2001; Ho & Newcombe 2005). However, the efficiency of PAC is attenuated by the presence of high levels of NOM. Therefore, high dosage is required for adequate removal, resulting in high operational costs. For example, a 15 d dosing of powdered activated carbon (PAC) to remove geosmin may cost up to

AUS\$27000 (Australia, based on a PAC dose of 20 mg/L for a 50,000 L/d plant at a price of \$1800 per ton PAC) (Ho 2004). The development of low-cost, high efficiency adsorbents for removing geosmin and MIB would be highly beneficial.

Fly ash is a finely divided and powdered by-product from coal or biomass fired power plants. Worldwide, there is approximately 500 million tons of fly ash to be disposed of annually. Bentonite, with 2.5 billion tons of deployable reserves, is also a readily available material. The cost of 1 ton of bentonite in China was approximately 180 Yuan (\$26.6/t) and the fly ash costs about 45 Yuan per ton (\$6.7/t), whereas the PAC costs about 5500 Yuan per ton (\$820.9/t). Consequently it would be advantageous to utilize these materials for reasons both environmental and economic. It has been reported that fly ash and bentonite can remove toxic metals (Wang *et al.* 2009); phenolic compounds (Akgerman & Zardkoohi 1996) and dyes (Janos *et al.* 2003). However, few investigations have been reported on the adsorption of MIB and/or geosmin. In this paper, we report using activated fly ash and bentonite as an adsorbent to remove MIB and geosmin from aqueous solution. The adsorption isotherm of a single pollutant and a bi-component are also investigated.

## MATERIALS AND METHODS

### Materials

#### Adsorbates

Standard substances of MIB and geosmin were both obtained from Wako Pure Chemicals Industries Ltd (Osaka, Japan) and prepared as a stock solution with concentration of 10 µg/L in methanol. The stock solutions were stored at 4 °C and were further diluted to 200 ng/L with ultrapure water (ELGA Lab Water) before immediate use. These solutions were working solutions for either MIB or geosmin single adsorbate.

MIB and geosmin used in the binary adsorption were prepared from actinomycetes, which were isolated from Lake Lotus in Wuhan, China and were cultured by the

method described by Zuo *et al.* (2009). The contents of MIB and geosmin were  $106 \pm 4$  and  $180 \pm 2$  ng/mL, respectively. The culture medium was filtered by a 0.2 µm membrane (Millipore) and kept at 4 °C before using. The filtrate was the working solution for binary adsorption.

### Raw materials

The natural bentonite used in this experiment was received from Ezhou Zhaoshan Bentonite Co., Hubei Province, China. Those fractions of less than 200 meshes were kept after grinding and screening. The gelatine, dilatibility, amount of methylene blue adsorption and cation-exchange capacity of natural bentonite were 45 mL/15 g, 15 mL/g, 34 g/100 g and 75.4 mmol/100 g, respectively. Fly ash was from Qingshan Thermal Power Plant of Hubei Province, China. The composition of the natural bentonite used was 65.18% SiO<sub>2</sub>, 17.42% Al<sub>2</sub>O<sub>3</sub>, 2.16% Fe<sub>2</sub>O<sub>3</sub>, 3.85% MgO, 1.72% CaO, 0.46% TiO<sub>2</sub>, 0.41% Na<sub>2</sub>O, 0.87% K<sub>2</sub>O and 7.93% LOI (loss on ignition). The natural fly ash was composed of 54.12% SiO<sub>2</sub>, 25.35% Al<sub>2</sub>O<sub>3</sub>, 8.36% Fe<sub>2</sub>O<sub>3</sub>, 1.15% MgO, 3.00% CaO, 0.49% TiO<sub>2</sub>, 0.22% Na<sub>2</sub>O, 0.93% K<sub>2</sub>O and 6.38% LOI. The average particle size of natural bentonite and fly ash was 6.1 and 20.5 µm, respectively.

### Methods

#### Adsorbent preparation

The hybrid of bentonite and fly ash adsorbent: an appropriate amount of bentonite powder was mixed in 20% (w/w) sulfuric acid for 0.5 h at ambient temperature while stirring, and then we added the calculated fly ash and stirred for another 0.5 h. The suspension was filtered off and then washed several times with ultrapure water until the pH was 7 and dried in an oven at 110 °C for 4 h prior to use.

Bentonite or fly ash: an appropriate amount of bentonite or fly ash was mixed in 20% (w/w) sulfuric acid for 0.5 h at ambient temperature while stirring. The suspension was filtered off and then washed several times with ultrapure water until the pH was 7 and dried in an oven at 110 °C for 4 h prior to use.

## Characterization of adsorbent

The XRD (x-ray diffraction) patterns of the adsorbent were recorded on a Rigaku D/MAX – IIIA (Japan) diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) radiation operating at 40 kV and 50 mA. The scanning range was from  $2\theta = 5\text{--}60^\circ$  with a scanning speed of  $1.5^\circ/\text{min}$ . The morphologic structure of the adsorbent was observed using a FEI Quanta 200 scanning electron microscope (SEM) (The Netherlands) operating at an accelerating voltage of 20 kV. The surface area and total pore volume of all the samples was measured by  $\text{N}_2$  adsorption on a JW-BK BET surface area analyzer (Beijing JWGB, China).

## Adsorption experiments

**Equilibrium isotherms:** The glassware was washed with ultrapure water and then oven-dried prior to use. At room temperature ( $25^\circ\text{C}$ ), the adsorbent was placed in a clean 250 mL conical flask and followed by the addition of MIB or geosmin solution for a single working solution or the actinomycetes culture for a binary working solutions. An initial adsorbate concentration of 42–234 ng/L was used for MIB and geosmin. An initial concentration of 10 mg/L humic acid (HA) was added to simulate the competing adsorption of NOM. The conical flask was sealed tightly with PTFE film and stirred for 4 h (Considine *et al.* 2001). The suspension was then centrifuged at 4,000 rpm for 10 min and the supernatant was retained for analysis of MIB and geosmin.

**Determination of optimal adsorption conditions:** The effects of fly ash to bentonite ratio, the time required to establish equilibrium, solution pH and adsorbent dosage were investigated. The optimal fly ash to bentonite ratio was determined by preparing a series of hybrid adsorbents with different mass ratios of fly ash to bentonite. The proportion of fly ash in the hybrid mixtures tested was 0, 25, 40, 50, 60, 75 and 100%. To determine the time required for equilibrium to be established, adsorption was measured after contact times of 15, 30, 45, 60, 90 and 120 min. The optimal adsorption pH was determined by measuring adsorption at pH values of 6, 7, 8 and 9. The pH of the solution was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl. The adsorbent and actinomycetes

culture medium were added to the conical flask and continuously stirred for 15–120 min. Adsorbent doses included 5, 10, 15, 20 and 25 mg/L. An initial adsorbate concentration of 42–234 ng/L was used for MIB and geosmin.

## MIB and geosmin analysis

Analysis of MIB and geosmin was carried out using headspace solid phase micro-extraction (HSPME)/gas chromatography (Shimadzu GC-17A) (Zuo *et al.* 2010).

## Heavy metal leaching experiment

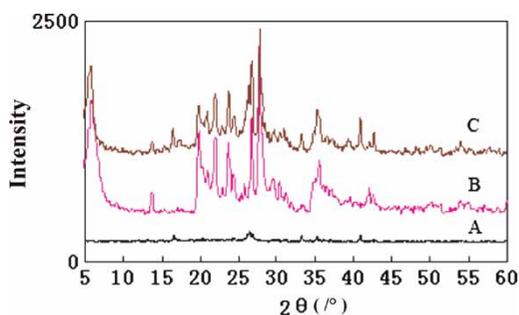
The concentrations of Pb, As, Hg, Cr, Cd, Mn and Cu of the supernatant from the equilibrium adsorption experiment were analyzed by an atomic absorption spectroscopy graphite furnace (Varian SPECTRAA-240FS, atomization at  $2,100^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

### Characterization of adsorbents

The XRD patterns in Figure 1 indicate that the adsorbents have montmorillonite crystalline structures. The calculated montmorillonite basal spacing ( $d_{001}$ ) was 1.53 nm for activated bentonite and 1.56 nm for the bentonite of the hybrid adsorbent.

BET analysis in Table 1 gave a specific surface area of  $18.6 \text{ m}^2/\text{g}$  for natural bentonite and  $73.9 \text{ m}^2/\text{g}$  for



**Figure 1** | The x-ray diffraction patterns of the fly ash (A), bentonite (B) and the synthesized hybrid adsorbent (C). All the samples were activated by sulfuric acid.

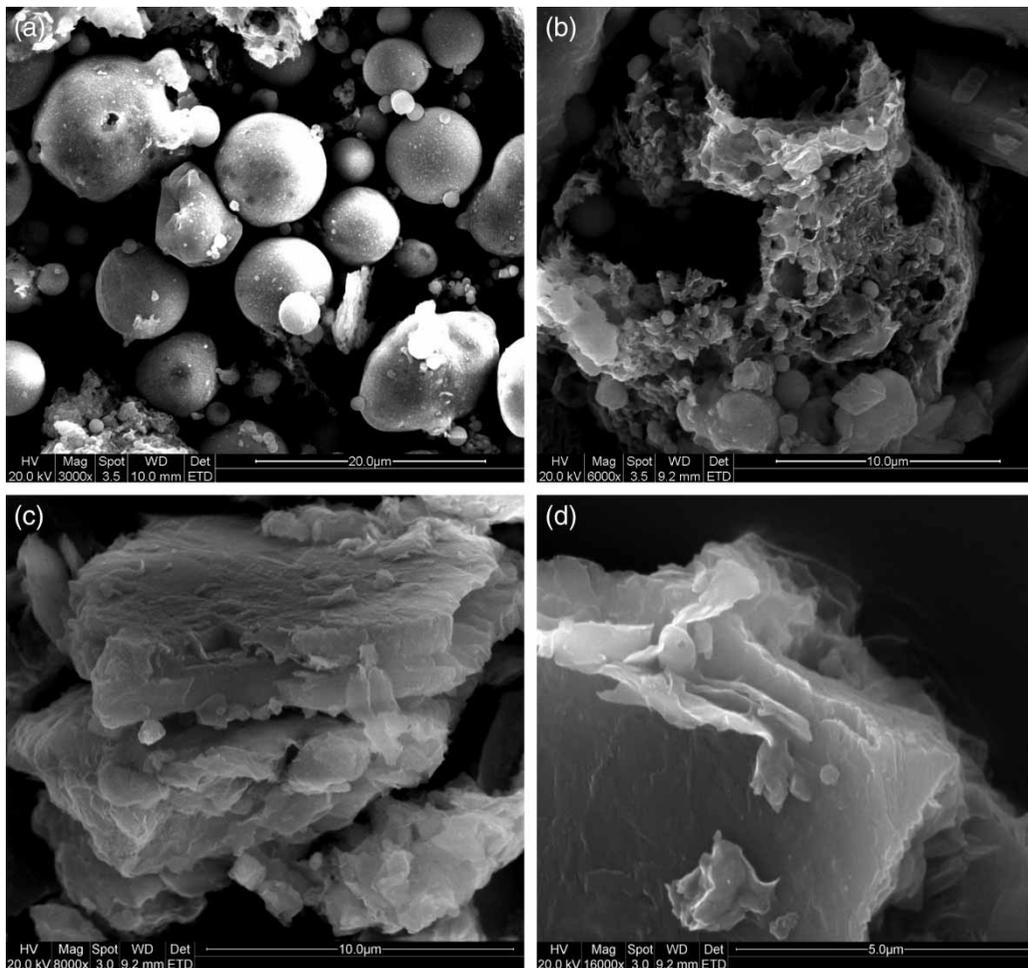
**Table 1** | Porous structure parameters of the five samples

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_t$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{mic}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{meso}}$ ( $\text{cm}^3/\text{g}$ )	$D_p^b$ (nm)
Natural fly ash	26.6	0.07	–	0.066	5.362
Natural bentonite	18.6	0.05	–	0.047	5.055
Acid-activated fly ash	66.4	0.10	0.002	0.099	4.864
Acid-activated bentonite	73.9	0.12	0.004	0.115	4.275
Hybrid adsorbent	63.5	0.12	0.007	0.112	4.366

acid-activated bentonite. The specific surface area of natural fly ash was  $26.6 \text{ m}^2/\text{g}$  and  $66.4 \text{ m}^2/\text{g}$  for acid-activated fly ash. The specific surface area of the

hybrid adsorbent was  $63.5 \text{ m}^2/\text{g}$  in a mixture containing 40% activated fly ash and 60% activated bentonite.

Figure 2 shows SEM images of the natural fly ash (a), natural bentonite (c), the activated fly ash (b) and the activated bentonite (d). As can be seen, the fly ash contained well-developed spherical particles with diameters of 5–20  $\mu\text{m}$  along with some irregularly shaped particles. The spherical particles may be hollow particles filled with smaller spheres. The smooth surface of the spheres became rougher upon acid etching, clear evidence of the increase in surface area produced by acid activation. The bentonite showed a typical layer structure after activation.

**Figure 2** | Scanning electron micrograph of the natural fly ash (a), the activated fly ash (b), the natural bentonite (c) and the activated bentonite (d).

### Effect of fly ash to bentonite ratio

The ratio of fly ash and bentonite played an important role in the physical and chemical characteristics of the hybrid adsorbent and affected adsorption behavior. The results are presented in Figure 3. When activated bentonite or fly ash alone was used as the adsorbent, the removal percentages were 25.7 and 36.7% for MIB and 34.3 and 31.4% for geosmin. However, the removal percentages of MIB and geosmin by the non-activated bentonite or fly ash were 14.5, 17.6 and 18.8, 19.1%, respectively. The removal percentages increased as the ratio of fly ash to bentonite increased from 0:1 to 0.4:0.6, reaching the maximum adsorption of MIB and geosmin of 45.4 and 49.6%, respectively, at a ratio of 0.4:0.6. Increasing the ratio further caused a decline in the adsorption of both. Bentonite and mixed adsorbent showed higher removal efficiency for geosmin than for MIB. The fly ash showed higher removal efficiency for MIB, indicating that the microstructure of bentonite favors the adsorption of geosmin and fly ash favors the adsorption of MIB.

### Adsorption time

The effect of adsorption time on the removal efficiency was shown in Figure 4. Kinetics is typical for adsorption processes; rapid initial adsorption for both MIB and geosmin with a declining rate as equilibrium is approached. Adsorption was near completion after 60 min of contact: 53.6% for MIB and 49.6% for geosmin.

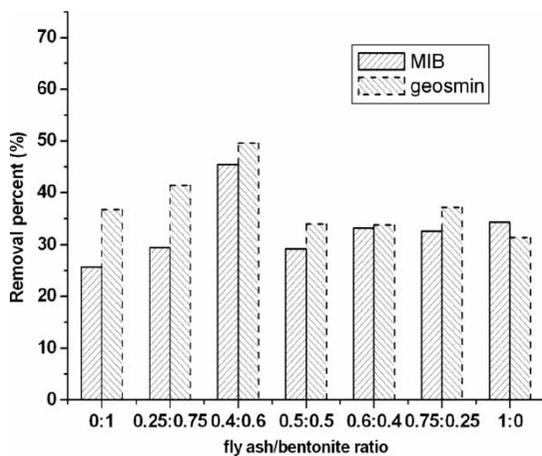


Figure 3 | Removal percent of adsorbent as a function of fly ash/bentonite ratio (20 mg/L dosage, pH 8).

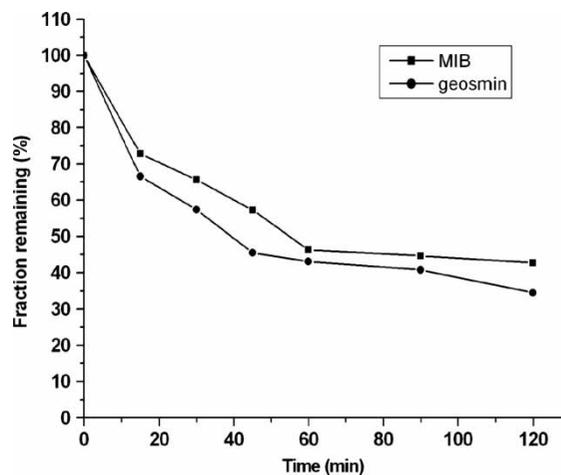


Figure 4 | Effect of contact time on the adsorption of MIB and geosmin by the adsorbent (20 mg/L dosage, pH 8).

MIB removal in the first 60 min, 3.6% removal in the following 60 min; 56.8% of geosmin removal in the first 60 min, 8.7% in the following 60 min.

### Effect of pH

To determine the pH effect on adsorption efficiency of the target compounds, solutions were prepared at different pH levels from 6 to 9 before adding the adsorbent. The pH of the water was varied by the addition of 0.1 mol/L HCl or 0.1 mol/L NaOH. As can be seen from Figure 5, removal efficiency of both compounds increased when the initial pH of the solution was increased from 6 to 8 and negligible

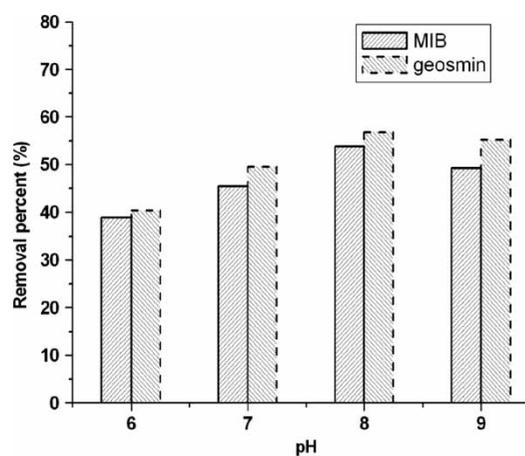


Figure 5 | Effect of pH on the adsorption of MIB and geosmin by the adsorbent dosage 20 mg/L.

difference was found in the adsorption from 8 to 9. Considering the alkalinity and pH of most surface waters, subsequent adsorption experiments were conducted at pH 8, fortunately similar to many eutrophic waters.

### Effect of dosage

The effect of dosage for either MIB or geosmin was determined by adding adsorbent levels ranging from 5–25 mg/L. The results, shown in Figure 6, indicate that increasing adsorbent dosage from 5–15 mg/L increases adsorption of MIB and geosmin up to 15 mg/L (giving removals of 59.9% for MIB and 63.7% for geosmin). Further increases in adsorbent dosage do not increase adsorption for MIB or geosmin. The reason may be due to adsorbent particle aggregation at higher dose levels leading to a decrease in total surface area of adsorbent and an increase in diffusion path length (Papachristou *et al.* 1985).

### Effect of NOM on the adsorption of MIB and geosmin

NOM adversely affects the adsorption of micropollutants, such as pesticides and taste and odor compounds due to competitive adsorption (Pelekani & Snoeyink 1999, 2001; Newcombe *et al.* 2002). As a consequence the adsorption of the micropollutants can be dramatically attenuated. The degree of the adsorption depends on a number of factors such as charge, size and polarity of the adsorbate, and the

relationship between the adsorbate structure and the surface of the adsorbent (Summers & Roberts 1988). The effect of NOM on the adsorption of MIB and geosmin by activated carbon has been comprehensively studied (Newcombe *et al.* 1997). To assess the impact of NOM on the adsorption of MIB and geosmin by the hybrid adsorbent, equilibrium adsorption experiments were conducted in simulated natural water. The results are shown in Figure 7 and indicated that the presence of NOM causes a small decline in the adsorption. In the simulated system, the concentration of humic acid was much higher than that of MIB and geosmin (about 100,000 times MIB and geosmin) (Newcombe *et al.* 2002). Therefore it is not surprising that the adsorption efficiency of the target compounds decreased. NOM is also adsorbed in the layered structure of bentonite and/or on the surface of the fly ash providing the competition for adsorption of MIB and geosmin. The results are consistent with the findings of Herzing *et al.* (1977) using activated carbon as adsorbent. Geosmin and MIB are partially displaced by humic acid on the surface of PAC. It was suggested that, due to the existence of high concentration of humic acid, the large pores of the PAC were occupied by humic acids, lowering the efficiency of activated carbon by occlusion of the larger pores and limiting the access to smaller pores. However, the presence of humic acid concentrations equivalent to 5 mg/L actually enhanced the adsorption efficiency of MIB and geosmin by ultrastable

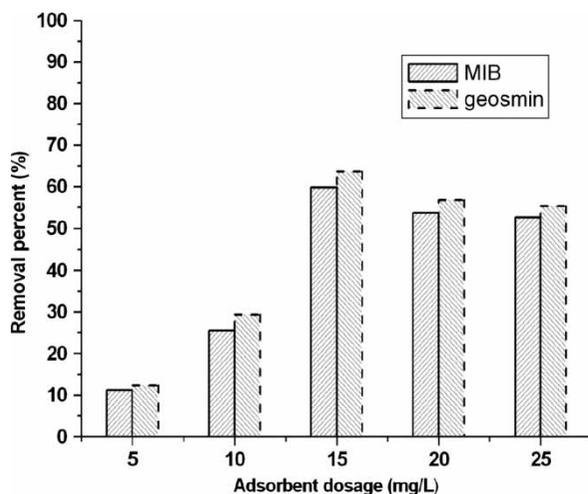


Figure 6 | Effect of the adsorbent dose on the adsorption efficiency of MIB and geosmin at pH 8.

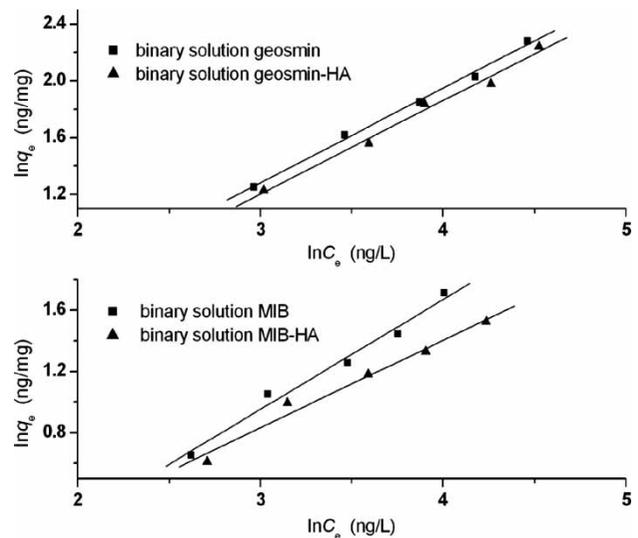


Figure 7 | Effect of 10 mg/L humic acid on the adsorption of MIB and geosmin by the adsorbent (15 mg/L dosage).

zeolite-Y (Ellis & Korth 1993), as humic acid is much too large to enter the pores of this adsorbent. The specific adsorption behavior was attributed to the high uniformity of pores.

### Explanation of the increased adsorption efficiency of the hybrid adsorbent

From the characterization of the adsorbent, it was noted that, after the activation by sulfuric acid, both the fly ash and bentonite showed higher surface area. For the fly ash, the surface area increased, which was in agreement with the literatures (Sarbak *et al.* 2004). For the bentonite, the surface area increased from 18.6 to 73.9 m<sup>2</sup>/g, which was similar to the findings of previous studies (Salem & Karimi 2009). The activation process eliminated the metal oxides or inorganic salts in the passage in favor of the diffusion of the adsorbates. Additionally, by activation by sulfuric acid, H<sup>+</sup> displaces Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> in the interlayer of bentonite, weakening the interlayer force and increasing adsorption capacity (Babaki *et al.* 2008).

From the XRD patterns the calculated montmorillonite basal spacing  $d_{001}$  was 1.53 and 1.56 nm for the activated bentonite and the bentonite of hybrid adsorbent, respectively. By subtracting 0.97 nm from the basal spacing of bentonite (Lagaly 1979), the interlayer distance of activated bentonite calculated from the basal spacing  $d_{001}$  was 0.59 nm, in accord with the molecular dimensions of MIB and geosmin (0.59 nm) (Pendleton *et al.* 1997). This favors access of MIB and geosmin to the adsorbent interior. However, before activation, the interlayer distance of 0.56 nm was not sized for the access and adsorption of both adsorbates.

### Leaching analysis

There are health concerns to be considered when using fly ash as the adsorbent for potable water treatment that include potential leaching of heavy metal elements such as copper, chromium, arsenic, mercury and cadmium. The results of the atomic absorption tests indicated that the concentration of lead, chromium and manganese were 0.0003, 0.0002 and 0.0006 mg/L, respectively, far below the acceptable limits in the standards of the USEPA (2006) and other international organizations (e.g. European (98-83-EC) and

WHO (3rd)). Other elements, such as copper, arsenic, mercury and cadmium, were beyond the limit of detection or not detected, which suggests that leaching of heavy metals is not of concern for this particular application. The high risk of heavy metal leaching may occur when the fly ashes were used directly as raw material. Generally the adsorbents prepared from some coal combustion fly ashes would leach toxic substances less than the standard values but other adsorbents prepared from other coal combustion fly ashes would leach toxic substances over the standard values. In the present study, the hybrid adsorbents were obtained by strong acid treatment and repeated washing, which could remove most of the heavy metals and reduce the risk.

### CONCLUSION

This investigation indicates that the synthesized hybrid adsorbent can be used as a low-cost adsorbent for removing trace amounts of MIB and geosmin. The highest removal efficiency for MIB and geosmin was obtained at the adsorbent dosage of 15 mg/L at pH 8.0 and a contact time of 60 min. Experimental data of the presence of NOM indicate adsorption decreased slightly. Leaching study results indicate that the concentrations of heavy metals for all samples were below the USEPA and other international organizations' limits. Comparing to PAC, the cost of the synthesized adsorbent was very low, implying that the adsorbent showed potential application in the removal of MIB and geosmin. Considering the low cost of the adsorbent and abundant materials and the negligible leaching of heavy metals, the hybrid adsorbent has excellent potential as a treatment for taste and odor problems caused by geosmin and MIB.

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