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Development of a ceramic adsorbent for the removal of 2-methylisoborneol from aqueous solution

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ABSTRACT

Removal of 2-methylisoborneol (2-MIB), a common musty odor compound, by a novel ceramic adsorbent (CA), developed with a mixture of akadama mud, wheat starch, and Fe_2O_3 is presented. The physicochemical characteristics of the CA are examined with scanning electron microscope (SEM), Energy Dispersive X-ray (EDX) and gas adsorption porosimetry analyses. The effects of initial 2-MIB concentration, contact time and initial solution pH are investigated. It is observed that the adsorption of 2-MIB by CA occurs by a pseudo-first-order mechanism. CA exhibits high removal efficiency for 2-MIB in both high (600 ng/L) and low (200 ng/L) initial 2-MIB concentrations at room temperature (25 °C) and can adapt to a wide range of pH (2–12) for 2-MIB adsorption. Over 80% of 2-MIB is removed by the CA within 600 min at an initial concentration of 200 ng/L with 20 g/L of CA dose. High regeneration performance shows that CA has great potential for reuse. These results suggest that the developed CA could be a promising material for effective and rapid removal of musty odor compounds in drinking water. Data on the adsorption kinetics and mechanism of adsorption are also presented.

1. Introduction

Taste and odor problems frequently occur in drinking water through out the world [1–5]. One of the most common musty odor compounds, 2-methylisoborneol (2-MIB, Table 1) can be produced by a number of cyanobacteria and actinomycetes in aquatic environment [6–8]. It causes undesirable tastes and odors and has a relatively low threshold of detection in humans (2.5 ng/L) [9]. Although the offensive odor compound is nontoxic, it can arouse psychosomatic effects, such as headaches, stress, or stomach upsets [9], which lead to huge consumer complaints and mistrust on the safety of the drinking water [10].

2-MIB is earlier reported to be difficult to remove by conventional water treatment methods, as processes such as flocculation, sedimentation and filtration are not efficient to 2-MIB and sometimes conventional water treatment processes can lead to lyse algal cells, resulting in the release of additional intracellular metabolites [10,11]. Moreover, advanced oxidation processes, such as chlorination and ozonation are also not completely effective [12,13]. Also, biodegradation processes such as biofiltration require a significant period of time due to acclimation, and greatly rely on the types of organisms present [11,14]. On the other hand, adsorption, with the advantages of easy process, high removal efficiency, and potential regeneration provides an excellent feasible alternative. Several studies have focused on adsorbents of activated carbon [15,16]. Though these provide advantages such as high surface area and removal efficiency, the costs of the activated carbon and associated facilities are high [17,18]. Hence, there is a need to develop a novel adsorbent that is cost-effective and can overcome the above stated shortcomings. To the best of our knowledge, currently, there is little information on the adsorption of 2-MIB using ceramic adsorbent. Here, we report a novel ceramic adsorbent for removing 2-MIB from water. This ceramic adsorbent is solid and cylinder shaped. Ceramic green compacts were prepared by cost-effective mixture materials consisting of akadama mud, wheat starch, and Fe2O3 powder. Akadama mud, a deposit of volcanic ash, is common and inexpensive in Japan.

2. Materials and methods

2.1. Materials

2-MIB standard material used in this study was purchased from WAKO pure Chemicals Ltd., Osaka, Japan. The procured 2-MIB sample of 20 mg was dissolved in methanol and diluted in Milli-Q water (Resistivity 18.2 MΩ.cm at 25 °C) prepared with a water purification system (Purelite PRB-001A/002A) supplied by Organo, Japan. The stock solution of 40 mg/L was transferred into 500 mL brown glass bottle with high gas tightness and stored in the dark at 4 °C prior to use.

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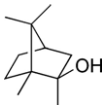
Table 1
Structure and physicochemical properties of 2-Methylisoborneol (2-MIB)[a].

Parameter	2-MIB
Structure	
Molecular formula	$C_{11}H_{20}O$
Molar mass (g/mol)	168.28
Boiling point (°C)	196.7
Aqueous solubility	194.5
Kow	3.13
Henry's law constant	$5.76*10^{-5}$

[a] Pirbazari et al. [30].

Akadama mud, a common, inexpensive deposit of volcanic ash, was provided by Makino Store, Kiyosu, Japan. The chemical composition was analyzed by semi-quantitative elemental analysis and element mapping by energy dispersive X-ray spectrometry (EDX). The results are presented in Table 2 and show that akadama mud is primarily a mixture of Si, Fe and Al oxides. Akadama mud was crushed and sieved to obtain fractions through a 177 μm screen. The particles below 177 μm were dried at 105 °C for 24 h and then used for the CA development. All chemical reagents, including the wheat starch (granule size: 1–5 μm) and iron oxide, used in this study were of analytical grade (Wako Pure Chemical Industries, Japan).

2.2. Synthesis of the ceramic sorbent

The sorbent was a mixture of the powders of akadama mud, wheat starch and Fe_2O_3, 56%:24%:20%, respectively. Fe_2O_3 was introduced as an additive for the content of iron, which could be prone to form hydroxylated complexes like ferric hydroxide that can enhance the high 2-MIB adsorption ability of the adsorbent. The ferric hydroxide is helpful for removal of the organic matter [19]. It is reported that the hydrous ferric oxide complexation is able to enhance the adsorption ability of many organic materials, such as, phthalic acid, phthalate, trimellitate, pyromellitate, and phosphate [20–22].The detailed process of preparing the adsorbent is described in our previous work [23].

2.3. Analytical methods

2-MIB concentration in the samples was quantitatively analyzed by gas chromatography–mass spectrometry system (GC/MS system) equipped with a pure and trap apparatus (P&G: O.I. Analytical 4660, Auto Sampler: O.I. Analytical 4551A, GC: Agilent Technologies 6890N, MS: Agilent Technologies 5973 inert). The detection limit was 1.0 ng/L 2-MIB. The GC column used was NB-1 30 m × 0.25 mm i.d. (0.25 μm film thickness). The carrier gas was helium with flow rate at 1.0 mL/min. The GC oven temperature program was as follows: hold at 40 °C for 7 min; raise to 200 °C (15 °C/min); raise to 280 °C (10 °C/min); the GC–MS transfer line temperature was maintained at 280 °C. The electron impact (EI) ionization mode was used with an electron energy of 70 eV.

Specific surface area and pore size distributions were determined by gas adsorption using a Brunauer–Emmett–Teller (BET) specific surface analysis device (Coulter SA3100, US). Morphological images before and after 2-MIB adsorption were acquired by SEM (JSM-6700F, JEOL, Japan). Local chemical analysis was conducted using SEM coupled with an Energy Dispersive X-ray (EDX) spectroscopic detector (SEM-EDX, JEOL, Japan). Solution pH was measured by pH S-3C precision pH/mV meter.

The experimental data for kinetic study are analyzed using a pseudo-first order Lagergren equation:

$$\log(q_e - q_t) = \log(q_e) - t*k_1 / 2.303 \quad (1)$$

where q_e and q_t are the amount of 2-MIB adsorbed at pseudo-equilibrium condition and at time t, respectively, and k_1 is the adsorption rate constant, which indicates the adsorption energy.

2.4. Experimental design

In the present study, batch adsorption experiment was conducted in order to obtain kinetic and equilibrium data. For kinetic study, 100 mL synthetic 2-MIB solutions (initial concentration: 200 ng/L) were spiked into a 300 mL conical flask. The adsorption was performed with a ceramic dosage of 2.0 g at (25 ± 1 °C) and a speed of 100 rpm. Solution samples were taken at the certain intervals (0, 10, 30, 60, 180, 360 and 600 min) and filtered through a 0.45 μm membrane filter for measurement of the 2-MIB concentration. The adsorption process was ceased when 10 h elapsed. Furthermore, solutions with different initial 2-MIB concentrations (200 and 600 ng/L) were prepared for assessment of adsorption ability by CA. The initial pH effects on 2-MIB adsorption were investigated by adjusting the pH value of the solution from 2 to 12 (adjusted by adding 1.0 M HCl or 1.0 M NaOH). The ionic strength influence of HCl or NaOH addition could be ignored (less than 1%). Finally, the used CA was subject to regeneration experiments.

3. Results and discussion

3.1. Sorbent characterization

Several adsorbents for 2-MIB removal have recently been reported [17,18,24], however, studies on 2-MIB removal by ceramics as sorbent are limited. This is the first report on 2-MIB removal by ceramic adsorbent. The BET specific surface area of the CA was found to be 38.19 m^2/g, and the pore volume was 0.0869 mL/g. The pore size distributions (Fig. 1) show that the observed pore sizes mostly varied between 2 and 50 nm (63.59%). According to IUPAC classification, ceramic is a typical mesoporous material. The results also indicated that a large percentage of the pores (19.86%) were under 2 nm, which is a favorite adsorption size for 2-MIB according to the previous reports. Newcombe et al. [25] found that 2-MIB adsorption was primarily related to the micropore volumes within the pore size range between 10 and 12 Å.

The EDX results (Table 2) show that the iron content of CA accounted for 27.68%. This implies that when compared with akadama mud, the proportion increased almost 4 times due to the addition of Fe_2O_3. High adsorption amount of organic substance is related to iron and iron oxide species [26]. This may be helpful for enhancement of formation of hydroxylated complexes.

The surface morphology of the CA was examined by a Scanning Electron Microscope (SEM). Fig. 2a and b presents the surface features of adsorbents before and after 2-MIB adsorption at a magnification of 200×. It can be seen that the iron oxides on ceramic granules surfaces initially form a rough surface structure (Fig. 2a). 10 h of water erosion during 2-MIB adsorption appears to have smoothened the surface structure (Fig. 2b). However, the pore structure shows no obvious

Table 2
Chemical analysis of akadama mud and ceramic adsorbent by SEM-EDX test.

Composition (wt.%)	Akadama mud	Ceramic adsorbent [a]
SiO_2	51.3	43.49
Al_2O_3	38.05	26.64
Fe_2O_3	7.67	27.68
MgO	1.94	1.52
CaO	0.78	0.49
MnO	0.26	0.18
pH_{zpc}	6.9 [b]	6.4 ± 0.2

[a] The effect on LOI (600 °C) has been neglected.
[b] Information supplied by the manufacturer.