Geosmin Sorption on Cyclodextrin Polymers

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ABSTRACT

Geosmin is one of the major causative compounds of earthy-musty odor and taste (off-flavor) in drinking water (lakes) and in farmed fish. In this study, the sorption of cyclodextrin polymers (CDPs) towards geosmin in aqueous solution was investigated. Sorption kinetics, the effect of solution pH and contact time on the sorption capability of α-, β- and γ-cyclodextrin polymers was discussed. Results disclosed that the sorption of geosmin by the CDPs followed the Ho and McKay kinetic mechanism with the liquid film diffusion as the rate-determining step. Both β-CDP and γ-CDP exhibit high removal efficiencies of 93.4% and 96%, respectively, within 240 minutes at 25°C and pH 7, whilst α-CDP was not effective, removing only 40% geosmin, at an initial concentration of 5 μg·L^{-1} and 5 g·L^{-1} of CDP dose. The cyclodextrin polymers can adapt to a wide range of pH from 3.0 to 11.0 for geosmin adsorption with pH 7.0 as optimum. Results indicate that these sorbents demonstrate significant potential in reducing the concentration of geosmin in water that presents taint problems in both drinking water and fish.

Keywords: Geosmin; Cyclodextrin Polymers; Water; Sorption Kinetics

1. Introduction

Off-flavor comprises one of the biggest problems in the drinking water industry and aquaculture. Geosmin (*trans*-1, 10-dimethyl-*trans*-9-decalol) is a naturally occurring germacranoid sesquiterpene, produced by several species of cyanobacteria (*i.e. Anabaena, Oscillatoria* and *Phormodium*) and actinobacteria (especially *Streptomyces*) that impart an earthy-musty odor to water and fish when present at extremely low concentrations [1]. It is one of the most common taste- and odor-causing compounds found in drinking water supplies and in freshwater aquaculture ponds.

The use of conventional treatment techniques such as flocculation, sedimentation and filtration, for the removal of geosmin from water are not effective [2]. Furthermore, electrochemical, biochemical or photochemical degradation are effective processes but expensive. Adsorption is a much better process, in terms of efficiency and economy, than other physical techniques mentioned above. It is one of two treatment methods that have been successfully employed by water treatment plants to remove geosmin, the other being oxidation by ozone.

Suitable adsorbents for water purification are continuously being developed and tested, and cyclodextrin polymers (CDPs) are one of these materials. Several variants of insoluble CDPs were intensively investigated and were found to be very effective in the removal of organic pollutants and heavy metals in water [3,4]. It is well known that cyclodextrins polymers (α-, β- and γ-cyclodextrins) form inclusion complexes with molecules having a suitable size and shape. Other than surface adsorption, the removal of organic pollutants from water with CDPs occurs primarily via the formation of these inclusion complexes [3]. In this paper, we report on the application of CDPs (α, β and γ forms) in the removal of geosmin from aqueous solutions.

2. Materials and Methods

2.1. Materials

Synthesized α-, β- and γ-CDPs were provided by Kankyo Kougaku Co., Japan and were used without further purification. Geosmin standard solution (2,000 mg·L^{-1} in methanol) was obtained from Sigma-Aldrich Chemicals Co., USA. Working standard solutions for calibration and spiking were prepared from standard stock solution (100 mg·L^{-1}) using Milli-Q water. Solid phase microextraction (SPME) fiber (50/30 µm) coated with divinylbenzene/carboxen/polymethylsiloxane (DVB/CAR/PDMS) was purchased from Supelco Co. (Bellefonte, PA, USA). All chemical reagents, including methanol and sodium chloride crystals, used in this study were of analytical grade (Labscan Asia Co. Ltd., Thailand).

2.2. Extraction and Analytical Methods

Residual geosmin in the spiked water samples was extracted using headspace SPME. A 50/30 µm DVB/CAR/PDMS SPME fiber was extended into the headspace of samples (10 mL aqueous solution) placed in a clear 20-mL straight-sided vial. Sodium chloride (1.9 g) and a polytetrafluoroethylene (PTFE)-coated stirring bar were added and the vial was sealed with an aluminum crimp cap fitted with PTFE-faced silicone septum. Extraction time was 15 minutes and extraction temperature was maintained at 65˚C with vigorous agitation. Geosmin concentration was quantitatively analyzed by gas chromatography-mass spectrometry (GC/MS) using a HP 6890 Network gas chromatograph equipped with a 5973 mass selective detector (Agilent Technologies, USA) by desorbing the fiber in the injection port under a splitless mode at 230˚C for 5 minutes.

Specific surface area and pore size distributions were determined by N_2 gas adsorption using a Brunauer-Emmett-Teller (BET) specific surface analyzer (Autosorb-1-MP Quantachrome, USA). Morphological images of CDPs were acquired by SEM (JSM-5410LV, JEOL, Japan).

2.3. Sorption Studies and Kinetics

Spiked standard geosmin solution (initial concentration: 5 ug/L) was prepared and pH-adjusted to 3, 7 and 11 using 1 M NaOH and 1 M HCl solutions. One-hundred milliliters of spiked geosmin standard solution was placed in a 250-mL conical flask, 500 mg each of dry cyclodextrin polymer (α-, β- and γ-CDP) was added and the flask securely covered. Three replicates were prepared for each pH level. A blank (without CDP addition) was included with each isotherm experiment to evaluate sorbate losses by mechanisms other than sorption. Sorption batch experiment was conducted in a thermostat horizontal shaker (WB14/SV1422, Memmert, Germany) set at 25˚C with an agitation of 100 rpm. Samples were collected at various contact times (0, 15, 60, 120 and 360 min) and filtered through a 0.45 µm membrane filter (Advantech, Japan). Residual geosmin was quantified using HS-SPME and GC-MS. The data obtained were used to calculate the sorption capacity of the CDPs by:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

where, q_e is the amount of geosmin adsorbed at equilibrium (mol·L^{-1}); C_0 is the initial concentration of geosmin solution (mg·L^{-1}); C_e is the geosmin aqueous concentration at equilibrium (mg·L^{-1}); V is the volume of geosmin solution used (L); and m is the mass of the sorbent used (g).

3. Results and Discussion

3.1. Effect of Contact Time

The influence of contact time on the sorption of cyclodextrin polymers toward geosmin is shown in **Figure 1**. The sorption amount increased evidently with the increase of contact time initially after the first 15 min. Thereafter, the rate of geosmin sorption on the 3 CDPs was found to be slow until the equilibrium was reached and remained constant. Pseudo-equilibrium is achieved after approximately 240 min with maximum geosmin removals of 40%, 93.4% and 96% by the α-CDP, β-CDP and γ-CDP, respectively. The results reveal that rapid surface attachment (physical sorption) of geosmin onto the polymers played a major role at the initial stage, which consequently led to a fast initial geosmin removal from the water especially for β-CDP and γ-CDP. With time, the active sites on the polymers surfaces gradually decrease and the sorption process becomes slow. Diffusion of geosmin into the polymer network (via mesopores and micropores) possibly took place at this stage causing the particles of CDPs to slowly swell in the solution, until the equilibrium was reached [5].

3.2. Effect of pH

The results presented in **Figures 2(a)** to **2(c)** indicate that sorption capacities of the CDPs slightly depend on solution pH. The sorption capacity varies slightly among the 3 pH values, which means that the CDPs can adapt to a wide range of pH for geosmin sorption from water. The values of the sorption capacity for geosmin on CDPs in pH 7 are slightly higher than the other two pH solutions and therefore, considered the optimal pH. The slight increase at pH = 7 could be due to some of CDP may get hydrolyzed, dissociated and reverted back to water-soluble cyclodextrin (CD), which in turn the geosmin molecule formed inclusion complex with CD, increasing the sorption effect. Due to this reason the sorption capacity is higher in pH = 7 [6].
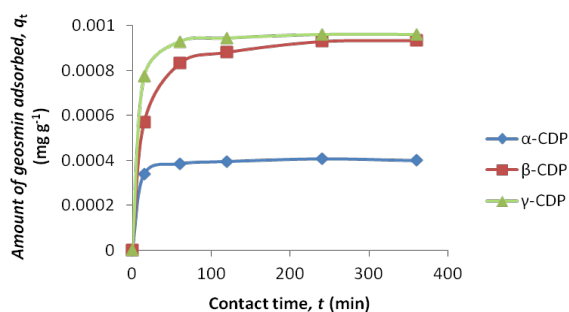

Figure 1. Effect of contact time on the sorption of geosmin (conditions: sorbent: 0.5 g; geosmin initial concentration: 5 µg·L^{-1}; volume: 100 mL; temperature: 25˚C; pH = 7).

3.3. Sorption Kinetics

The model equation used for fitting geosmin adsorption data was the Ho and McKay Model:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (2)$$

where, q_t and q_e are the amount of geosmin adsorbed at time t and at equilibrium (mg·g^{-1}), respectively; k_2 is the rate constant (g·mg^{-1}·min^{-1}). The values of k_2 and experimental $q_{e,expt}$ were calculated from the intercept and slope of the linear plots of t/q_t against t (**Figure 1(d)**). **Table 1** shows the calculated $q_{e,calc}$ from Equation 1, the results of kinetic fittings and the parameters associated with Ho and McKay model as well as the regression coefficients. Noteworthy are the high regression coefficients obtained from the plots and the high agreement between the calculated $q_{e,calc}$ and the experimental $q_{e,expt}$ values. This suggests the high applicability of the Ho and McKay model in describing the sorption process. Ho and McKay model follows the pseudo-second order mechanism, confirming that sorption of geosmin on CDP was complex, probably initially dominated by surface sorption (physical adsorption, hydrogen bonding) and thereafter, diffusion into the polymer network, chemisorptions via the formation of an inclusion complex due to the presence of the CD sites [7,8].

3.4. Rate Limiting Step in Sorption Process

To further interpret the sorption process, the moving boundary model [9-11] was used to discriminate the relative importance of adsorption steps involved to play in the pseudo-second order kinetic model. If the adsorption process was controlled by liquid film diffusion, intra-particle diffusion or chemical interaction, the rate constant can be expressed by Equation (3), (4) and (5), respectively.

$$k = -\ln(1-F) \qquad (3)$$

$$k = 1 - 3(1-F)^{2/3} + 2(1-F) \qquad (4)$$

$$k = 1 - 1(1-F)^{1/3} \qquad (5)$$

where F is the adsorption fraction (q_t/q_e), and k is the

Table 1. Ho and McKay sorption kinetic parameters of CDPs for geosmin (conditions: sorbent: 0.5 g; geosmin initial concentration: 5 µg·L^{-1}; volume: 100 mL; temperature: 25°C; pH = 7).

Sorbent	$q_{e,calc}$ (10^{-4}) (mg·g^{-1})	$q_{e,expt}$ (10^{-4}) (mg·g^{-1})	k_2 (g·mg^{-1}·min^{-1})	R^2
α-CDP	4.0	4.1	2997.7	0.9869
β-CDP	9.3	9.5	162.3	0.9993
γ-CDP	9.6	9.7	492.5	0.9999

(a)

(b)

(c)

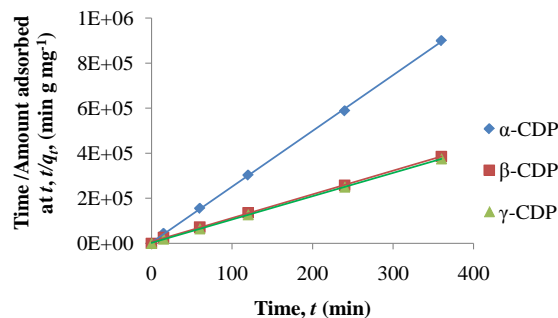**Figure 2. Effect of pH on sorption of geosmin on α-CDP (a), β-CDP (b) and γ-CDP (c).**

Figure 3. Ho and McKay plots for sorption of geosmin on CDPs (D) (conditions: sorbent: 0.5 g; geosmin initial concentration: 5 µg·L^{-1}; volume: 100 mL; temperature: 25°C; pH = 7).

sorption rate constant. By plotting a linear relationship of k versus contact time t (min) (**Figure 4**), the regression coefficients (R^2) for the three sorption steps were obtained, of which the one with the highest R^2 value was assumed to be the rate controlling step [11]. Result shows that the sorption of geosmin on the CDPs exhibited the highest regression coefficients for Equation (3) (**Table 2**), indicating that liquid film diffusion was the rate controlling step. Similar findings were reported by Li *et al.* [5] who found that film diffusion, and neither particle diffusion nor chemical interaction, was the rate limiting step in the sorption process of CDPs for 2,4-dichlorophenol. Noteworthy, geosmin has comparable hydrophobicity with 2,4-dichlorophenol, having an octanol-water partition coefficient (log K_{ow}) of 3.57 as compared to the latter's 3.06.

3.5. Sorption Capacity and Characteristics of CDPs

The different extents of geosmin sorption among the 3 CDPs may be attributed to BET specific surface area, pore size distribution and the inclusion effect between the sorbent and the sorbate. However, previous studies on CDPs [12,13] showed that BET specific surface area does not play an important role in the sorption process, which is in agreement with the BET result. BET surface area and total pore volume of γ-CDP are larger than α-CDP and β-CDP, so the sorption capacity of geosmin on γ-CDP is higher than that of α-CDP and β-CDP. However, α-CDP had the lowest sorption capacity among the CDPs despite its higher surface area and total pore volume than β-CDP (**Table 3**). Total pore volumes of the CDPs are quite low which ranged from 0.0108 to 0.0139 $cm^3 \cdot g^{-1}$. SEM micrographs of the CDPs (**Figure 5**) show their spherical morphologies with a rather smooth surface and low porosity. The pore size distributions (**Figure 6**) show that the observed pore sizes mostly varied between 1.5 and 10 nm. Pore sizes of 2 - 50 nm are classified as mesopores, whilst pore sizes of less than 2 nm are micropores. The results also indicated that a large percentage of the pores in γ-CDP (60%) were under 2 nm, which are a favorite adsorption size for geosmin (and 2-methyisoborneol) according to previous reports [14]. The sized-matched structure of geosmin relative to these pores could have contributed to γ-CDP's high sorption capacity. The sorption mechanisms of CDP are believed
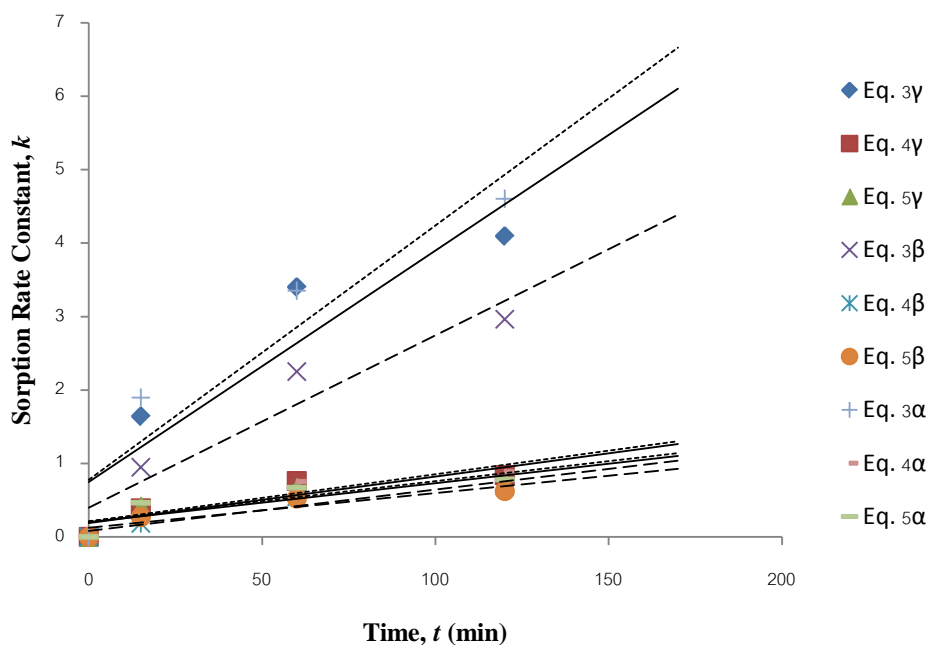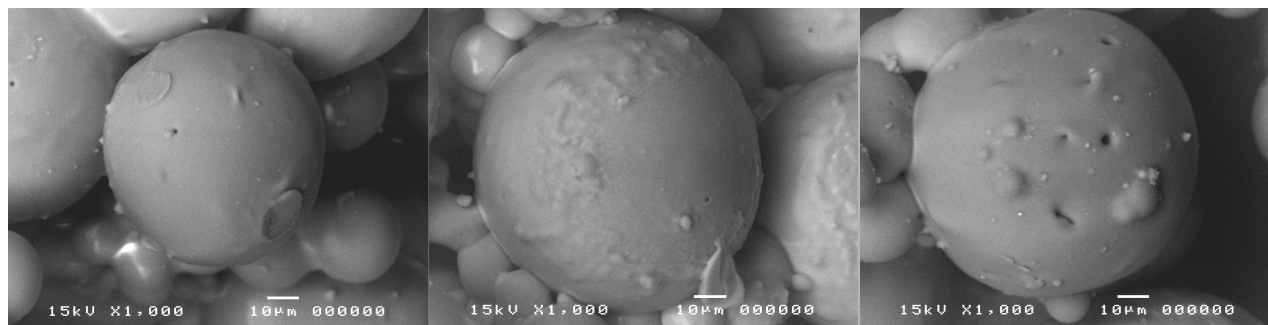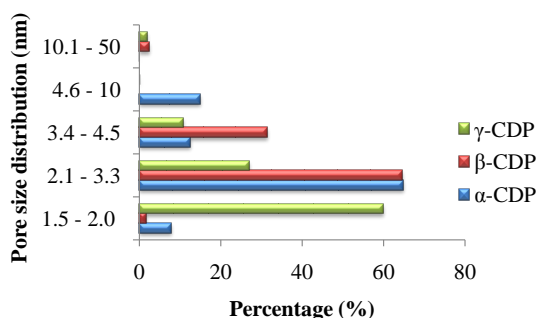

Figure 4. Plots of Equations (1), (2) and (3) for geosmin sorption on CDPs.

Table 2. Regression coefficient (R^2) fitted by moving boundary model for geosmin sorption on CDPs.

Sorbent	Equation (3) (liquid film diffusion)	Equation (4) (intra-particle diffusion)	Equation (5) (chemical interaction)
α-CDP	0.8879	0.7793	0.7242
β-CDP	0.9128	0.9096	0.8338
γ-CDP	0.8516	0.7873	0.7259

Table 3. BET specific surface area and pore properties of CDPs.

Sorbent	BET Surface Area, S ($m^2 \cdot g^{-1}$)	BET C-constant	Total pore volume, V_p ($cm^3 \cdot g^{-1}$)	Average pore radius (Å)
α-CDP	3.07	14.09	0.0118	77.08
β-CDP	1.82	50.60	0.0108	121.70
γ-CDP	5.37	4.36	0.0139	51.94

Figure 5. SEM images of α-CDP (A) β-CDP (B) and γ-CDP (C).

Figure 6. SEM images of α-CDP (A) β-CDP (B) and γ-CDP (C).

to involve physical sorption on surface and network, hydrogen bonding and inclusion complexation [15]. It is possible that the inclusion effect was strongest in γ-CDP and weakest in α-CD which is dependent on the molar content of CD units in the CDPs.

4. Conclusion

The result of this study indicates that β-CDP and γ-CDP are effective sorbents for the removal of the taste and odor compound, geosmin, from water. The optimum parameters for equilibrium study at a 0.5 g sorbent dose are time of contact 240 min and pH 7. Sorption kinetics of geosmin by the CDPs followed the Ho and McKay model (pseudo-second order) and the rate limiting step in the process of sorption was film diffusion. The high goodness of fitting for the pseudo-second order model could be ascribed to the nature of cyclodextrin-based polymers with multiple adsorption sites, which are responsible for different adsorption steps. The differences in sorption of geosmin by the CDPs could be attributed to the size-match structure of geosmin relative to the polymers' pores. Future work is required to evaluate the performance of the CDPs' in different types of natural waters to further address the challenges facing the water and aquaculture industries.

5. Acknowledgements

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