Adsorption Properties of Bamboo Charcoal and β-cyclodextrin on Volatile Organic Compounds

Yong-chun LIU¹,*, Ya-jun Li², Ying-ying Li¹, Hui-li Qi¹, Ke-jun ZHANG¹, Rui-xia LEI¹, Xu-dong ZHENG¹ and Yan QIN²

¹College of Chemistry and Chemical Engineering, FLUOBON Collaborative Innovation Center, Longdong University, Qingyang, Gansu 745000, P.R. China
²No. 203 Research Institute of Nuclear Industry, Xianyang, Shanxi 712000, P.R. China

*Corresponding author

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Abstract. The adsorption efficiencies of equimolar amount of beta–cyclodextrin (β-CD) on aqueous solution of 14 commonly volatile organic compounds (VOCs), including benzene, toluene, p-xylene, m-xylene, o-xylene, chlorobenzene, bromobenzene, ethyl benzene, styrene, 1,1-dichloroethene, trans-1,2-dichloroethene, cis-1,2-dichloroethene, trichloroethene and tetrachloroethene, were studied by UV-vis spectrophotometry, respectively. The results showed that the adsorption coefficient (α₁) of β-CD on benzene series had a good exponential relationship with its solubility in water (cₒ), α₁ = 1.104cₒ−0.44, R² = 0.868. The adsorption efficiency of β-CD on chloroalkenes was better than that of benzene series. Moreover, the higher the terminal distribution of charge of VOC molecule was, the higher the adsorption efficiency of β-CD on them. However, adsorption efficiency of bamboo charcoal on these VOCs was much lower than that of β-CD. Depending on the biotrickling filtration equipment containing bamboo charcoal as the growth medium for microorganism, the treatment efficiencies of styrene and odor by adding β-CD were increased to 95.47% and 71.77%, and increasing rates by 4.50% and 3.76%, respectively. This study provides a new synergistic idea and method for the treatment of VOCs by biological trickling filter combined with β-CD.

Introduction

With the large-scale development of industrial production, volatile organic compounds (VOCs) emitted by production sources have become an important part of air pollution in cities and key industrial areas, and may cause environmental air toxicity, which directly threatens human health and safety [1]. The composition of VOCs species is complex, involving alkanes, unsaturated hydrocarbons, benzene series, alcohols, aldehydes, ketones, esters, halogenated hydrocarbons and other species. In the US, 33 of the 187 pollutants that are first controlled by EPA belong to VOCs. Among them, benzene, trichloromethane and tetrachloroethylene have been identified by WHO as carcinogenic and teratogenic substances [2]. Different VOCs governance methods have their own scope of application, and the principles of governance are mainly recycling and emission reduction. For the low concentration VOCs without recycling value, destruction technology may be used, including catalytic oxidation technology, regenerative oxidation technology (RTO), biological method, thermal power incineration and low temperature plasma technology [3].

Biological methods are widely concerned with the advantages of simple equipment, low cost, good effect and simple operation. However, the efficiency of biological method to remove water-insoluble VOCs is very low, mainly because the mass transfer from gas phase to liquid is blocked [4]. In the traditional biological method, the hydrophobic VOCs from the gas phase through the liquid membrane to biofilm exists greater resistance in the process of mass transfer, thereby reducing the bioavailability [5], and this has become the main factors of restricting the microbial capture and degradation of VOCs. Wind drying experimental study taking up toluene as an example found that...
medium water holding capacity decreased after the biofilm surface water film thinning or disappearing reduced water film resistance, improving mass transfer rate of gas phase toluene and oxygen to the biological phase, and improving the rate of biomass degradation in the biofilm, but too low water will affect the bioactivity in biological trickling filter [6]. Studies also have shown that the resistance is mainly concentrated in the liquid phase during the gas-liquid mass transfer process, and the resistance of the water film accounts for about 96.3% for toluene [7]. Therefore, how to reduce the mass transfer resistance of VOCs between gas and liquid in the biological trickling filter system, so that the water is not only conducive to the growth of microorganisms, but also does not reduce the mass transfer rate of VOCs and oxygen to the biofilm, is one of the key problems to be solved by biological trickling filter for the treatment of hydrophobic VOCs.

Surfactant based hydrophilic and lipophilic groups can reduce the surface tension of liquid phase, increase water-solubility of organic matter, further reduce the mass transfer resistance and increase its bioavailability and other related properties [8]. However, chemical surfactants in the process of production and use often lead to environmental pollution. Some chemical surfactants are toxic and their biodegradability is poor. Also it is possible to introduce secondary pollution into environment [20]. Bio-surfactant as an environmentally friendly natural surfactant, has the same surface activity effects of reducing the surface tension, stabilizing emulsion and increasing foam as chemical agent, also has the efficient surface activity or emulsifying activity, low toxic or non-toxic, biodegradable, some bio-surfactant have better tolerance to extreme temperature, pH and salinity conditions [9, 10].

Cyclodextrin (CD) is a cyclic oligosaccharide formed by 6–12 D-glucosyl groups with alpha-1,4-glucoside bonds, which is produced from cyclodextrin glucosyl transferase (CGT ASE) Bacillus acting on starch, glycogen and maltooligosaccharide. The more research molecules with important practical significance are molecules containing 6, 7 and 8 glucose units, called alpha cyclodextrin, beta cyclodextrin, gamma cyclodextrin, cavity sizes about 5, 7.8 and 9.5 Å, respectively [11], in which beta cyclodextrin (β-CD) is most widely used. The lateral frame of β-CD molecule is hydrophilic, and the inner cavity forms a hydrophobic region with volume of the cavity 0.346 nm³ [12]. β-CD has no toxic and side effects to the human body. It is a highly safe substance. β-CD molecules with unique barrel structure and like molecular bag can combine many inorganic and organic molecules into host-guest inclusion complexes, and can change the chemical and physical properties of encapsulated complexes of guest molecules, present the characteristics of protection, stability, solubilization, slow-release effect and selective molecular orientation of guest molecules [13]. This paper will explore the adsorption properties of bamboo charcoal and β-CD on some hydrophobic VOC molecules. In addition, depending upon related facilities of biofilter disposal of malodorous gases in a sewage treatment station, collaborative disposal efficiencies of biotrickling filter and β-CD for styrene odor will be studied.

Materials and Methods

Materials

Beta-cyclodextrin is of biochemical reagent. All of the volatile organic compounds (VOCs) involved are of analytical reagents. The experimental water is deionized water. Bamboo charcoal is of commercial substance purchased by Zhejiang shareholding Co., Ltd of China.

Methods

Equipped with a series concentration of VOCs solution of c, the absorbance A at maximum absorption wavelength of different concentration was recorded using UV-visible spectrophotometer (SPECORD 50, 1 cm quartz cell), then the A-c standard curve of A versus c was obtained. Referring to the VOCs solubility in water [14], equimolar amount of β-CD was added into a 50 mL saturated aqueous solution of VOC, then it was placed in a gas bath thermostat oscillator (CHA-S) under the condition of constant temperature 25 °C and shocked for 30 min. The molar adsorption coefficient (α₁)
of VOC by β-CD was calculated (refer with: Eq. 1) [15] and the mass adsorption capacity ($\alpha_2$) was calculated according to the molar mass of VOC involved and molar mass of β-CD (1135 g/mol).

$$\alpha_1 = (c_0 - c_1)/c_0. \quad (1)$$

Where $\alpha_1$ is the molar adsorption coefficient, that is, the mole amount of VOC adsorbed by per mole of β-CD, $c_0$ is the saturated concentration of a certain VOC in water, and $c_1$ is the tested VOC concentration after adsorption by β-CD.

Washed by deionized water and dried at 105 °C in an oven for 8 h, about 7 g of bamboo charcoal was filled in a drying tube. Then it was equipped with a flask containing 30 mL of a certain VOC. After heating up to the boiling point of VOC and keeping for 30 min, then cooled down and keeping for 6 h at a constant temperature 25 °C by a water bath, this bamboo charcoal adsorbing VOC was washed three times by 15 mL of cyclohexane, added washing solutions together, and the penetrable mass adsorption capacity ($\alpha_3$) of bamboo charcoal on a certain VOC was calculated according to the $A$-$c$ standard curve.

Depending upon related facilities of biofilter disposal of malodorous gases in a sewage treatment station, in which biological treatment tank was filled with bamboo charcoal as supporting medium for reproduction and film hanging of microorganisms, collaborative disposal efficiencies of biotrickling filter for styrene in the absence and presence of β-CD were tested respectively for 3 days and 12 times using gas chromatograph (GC 7900, Shanghai) and referring to GB/T 14677-93 [16], meanwhile odor was tested by triangle odor bag method referring to GB/T 14675-93 [17].

Results and Discussion

The Adsorption Efficiency of β-CD on VOCs in Water Ssystem

Figure 1 shows the UV-vis spectra and the standard curve for trichloroethylene in the solution of cyclohexane. Then the adsorption efficiency of β-CD on trichloroethylene is calculated. In the same way, the adsorption efficiencies of β-CD on other VOCs (spectra unlisted) can be calculated as shown in Table 1.

![Figure 1. The UV-vis spectra and the standard curve for trichloroethylene in the solution of cyclohexane.](image)

The plot of adsorption coefficient ($\alpha_1$) of β-CD on 9 benzene series VOCs versus its solubility in water ($c_0$) at 25 °C is shown in Figure 2. It is found that the adsorption coefficient of β-CD on these benzene series VOCs has an exponential relationship with the change of $c_0$, i.e., $\alpha_1 = 1.104c_0^{-0.44}$ ($R^2$...
which may be conducive to predict the adsorption coefficient of β-CD on other hydrophobic VOCs.

Although the adsorption coefficient of β-CD on chloroalkenes does not present good mathematical relationship with its solubility in water, but the adsorption efficiencies of chloroalkenes by β-CD are obviously better than that of benzene series, which may be related to smaller size of chloroalkene molecules. The adsorption coefficient order of anti-1,2-dichloroethylene < cis-1,2-dichloroethylene < 1,1-dichloroethylene suggests that the higher the charge distribution at the end of molecule is, the higher adsorption efficiency of the molecule by β-CD.

Table 1. Adsorption efficiency of β-CD on VOCs in aqueous solution at 25 °C.

<table>
<thead>
<tr>
<th>VOCs</th>
<th>$\alpha_1$ (mol/mol)</th>
<th>$\alpha_2$ (mg/g)</th>
<th>$\alpha_3$ (mg/g)</th>
<th>Solubility of VOCs in water $c_o$ (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.3325</td>
<td>22.88</td>
<td>7.354</td>
<td>22.53</td>
</tr>
<tr>
<td>toluene</td>
<td>0.3950</td>
<td>32.07</td>
<td>3.522</td>
<td>5.88</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>0.5375</td>
<td>53.30</td>
<td>2.492</td>
<td>3.47</td>
</tr>
<tr>
<td>styrene</td>
<td>0.6025</td>
<td>55.29</td>
<td>1.071</td>
<td>3.09</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>0.7232</td>
<td>100.0</td>
<td>4.510</td>
<td>2.61</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.8250</td>
<td>77.17</td>
<td>4.846</td>
<td>2.08</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.9709</td>
<td>90.82</td>
<td>0.1956</td>
<td>1.90</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.9754</td>
<td>91.24</td>
<td>0.4708</td>
<td>1.64</td>
</tr>
<tr>
<td>ethyl benzene</td>
<td>0.9550</td>
<td>89.33</td>
<td>1.840</td>
<td>1.55</td>
</tr>
<tr>
<td>anti-1,2-dichloroethylene</td>
<td>0.9678</td>
<td>82.66</td>
<td>0.4207</td>
<td>65.0</td>
</tr>
<tr>
<td>cis-1,2-dichloroethylene</td>
<td>0.9755</td>
<td>83.32</td>
<td>0.07658</td>
<td>36.10</td>
</tr>
<tr>
<td>1,1-dichloroethylene</td>
<td>0.9893</td>
<td>84.50</td>
<td>3.670</td>
<td>2.17</td>
</tr>
<tr>
<td>trichloroethylene</td>
<td>0.9753</td>
<td>112.9</td>
<td>4.147</td>
<td>8.372</td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>0.8868</td>
<td>129.6</td>
<td>0.5342</td>
<td>0.9045</td>
</tr>
</tbody>
</table>

Figure 2. Plot of adsorption coefficient ($\alpha_1$) of β-CD versus solubility of benzene series VOCs in water ($c_o$) at 25 °C.

In addition, bamboo charcoal present a certain adsorption capacity for VOCs mainly due to dispersion force and other weak intermolecular forces [18,19], however, the penetrable adsorption coefficient ($\alpha_3$) of bamboo charcoal for VOCs is much lower than that of β-CD, may be due to the lager cavity and small specific surface area of bamboo charcoal, in which the large cavity act as a channel [20].

The Collaborative Disposal Efficiency of Biotrickling Filter for Styrene in the Presence of β-CD

Depending upon biofilter tank of disposal of malodorous gases in a sewage treatment station, the average concentration of styrene of inport tested is 0.3729 mg/m$^3$, while the average concentration of exhaust port is 0.03367 mg/m$^3$, and the average disposal efficiency for styrene is 90.97%. It draws a
conclusion that the disposal efficiency of biofilter tank for odor is mainly due to the microbial degradation according to the adsorption coefficient ($\alpha_3$). In order to further improve the disposal efficiency of styrene, 43.85 g (0.03863 mol) β-CD per day is required to add into the circulating water tank on the basis of the adsorption coefficient of β-CD for styrene 0.6025 and the actual air flow rate 3000 m$^3$/h of biofilter tank. Then in the presence of β-CD, the average concentration of styrene of inport testd is 0.3804 mg/m$^3$, the average concentration of exhaust port is 0.01725 mg/m$^3$, and the average disposal efficiency for styrene is 95.47%, increased by 4.50% as shown in Figure 3, while the average disposal efficiency for odor increases to 71.77% and increasing rate by 3.76%.

![Graph](image)

**Figure 3.** Monitoring results of organized styrene in presence and in absence of β-CD in biotrickling filtration equipment.

### Summary

The adsorption efficiencies of bamboo charcoal and β-CD on 14 common VOCs were studied by UV-vis spectrophotometry, respectively. The results show that the adsorption efficiency of β-CD on VOCs is obviously better than that of bamboo charcoal. The adsorption coefficient of benzene series by β-CD has a good exponential relation with its solubility in water. This formula has a certain reference value for predicting the adsorption efficiency of other VOCs by β-CD. The adsorption efficiency of chloroalkenes by β-CD is obviously better than that of benzene series. Moreover, the higher the terminal charge distribution of VOC molecule is, the higher the adsorption efficiency of β-CD. Based on the biotrickling filter, the experimental results show that after the addition of β-CD, the treatment efficiencies for styrene and odor are increased to 95.47% and 71.77%, and the handling rates increased by 4.50% and 3.76%, respectively. This study provides a new synergistic idea and method for treatment of VOCs by the biological trickling filter combined with β-CD.

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