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# Adsorption kinetics and thermodynamics of yeast β-glucan for off-odor compounds in silver carp mince

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Methanol (PubChem CID: 887)
Sodium chloride (PubChem CID: 5234)

ABSTRACT

Yeast β-glucan (YG) adsorbs off-odor in silver carp mince due to its more porous structure. To explore adsorption behavior and mechanism, adsorption kinetics and thermodynamics of YG for 3 off-odor compounds (hexanal, 1-octen-3-ol and nonanal) were investigated by pseudo-first/second-order models and isothermal equations (Langmuir, Freundlich and Redlich-Peterson). Kinetic experiments indicated adsorption process followed pseudo-first-order model. Adsorption isotherms indicated 3 off-odors could easily be adsorbed by YG and adsorption capacity was in the order of 1-octene-3-ol > hexanal > nonanal. Thermodynamic result suggested adsorption of 3 off-odors by YG was endothermic and spontaneous, and was driven predominantly by physisorption and hydrophobic interaction. Consequently, the contents of 3 off-odors that released from mince/YG complex decreased by 22.8%, 29.9%, and 24.5% ($p < 0.05$), respectively, compared with those from mince without YG. Therefore, the addition of YG enhanced the binding capability to off-odors, thus reducing the release of off-odor from silver carp mince.

## 1. Introduction

Silver carp (*Hypophthalmichthys molitrix*), a freshwater fish, acts as a good source of a high quality nutritious protein, and can be processed into excellent white color surimi (Fu, Lin, Xu, & Wang, 2015). However, silver carp is susceptible to lipid oxidation, enzymatic reactions, microbial degradation, thus easily generating disagreeable off-odor during processing and storage (Eymard, Baron, & Jacobsen, 2009; Maqsood & Benjakul, 2011). The fishy off-flavor has been reported to be mainly due to hexanal, nonanal, 1-octen-3-ol, 2, 4-heptadienal (*E,E*), etc., produced from lipid oxidation (Fu, Xu, & Wang, 2009; Yarnpakdee, Benjakul, Nalinanon, & Kristinsson, 2012). Geosmin and 2-methylisoborneol are the major causes of earthy-musty odor in aquacultured fish, and they derived from the secondary metabolite of actinomyces and benthic algae in aquaculture water (Selli, Prost, & Serot, 2009). Trimethylamine (TMA) that has a strong fishy odor with a low sensory threshold originated from the precursor TMA oxide, and TMA oxide was abundant in marine fish (Baliozuazo & Barrancoauthor, 2016). Thus, the off-odor in fish meat has become the bottleneck to hinder the development of the surimi industry.

Many approaches such as chemical, biological and physical deodorization have been utilized to remove or reduce off-odor in fish products (Chen et al., 2016). Incorporating antioxidants into fish meat and oxidizing the off-odor compounds are effective chemical methods to reduce off-odors (Yarnpakdee et al., 2012; Zhang et al., 2016). However, these chemical methods may alter the compound composition or generate other substances. Biological methods, primarily referring to fermentation, can produce unique odor in aquatic products (Cai et al., 2017). But the fermentation might greatly influence physiochemical properties of fish product due to protein denaturation and degradation (Sun et al., 2016). Adsorption by powdered activated carbon (PAC) is a feasible physical method to remove off-odor. PAC shows excellent adsorption ability owing to its huge surface area and large number of tiny pores (Pan et al., 2018), but PAC is applicable for the deodorization of atmosphere and liquid products, rather than solid products such as fish meat products.

Yeast β-glucan (YG) obtained from the cell walls is a kind of water-insoluble polysaccharides, and it is composed of the β-(1 → 3)-glucan backbone branched with β-(1 → 6)-glucan sidechains (Klis, Mol, Hellingwerf, & Brul, 2003). YG has a broad spectrum of biological

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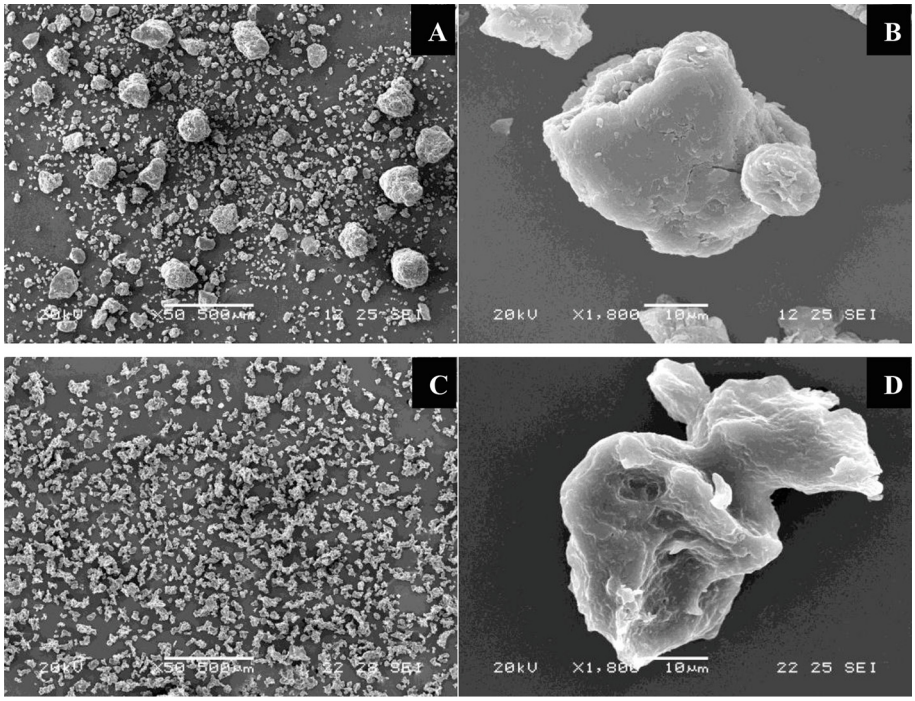


**Fig. 1.** SEM photographs of untreated (A and B) and hot water-treated (C and D) YG.

functions including anti-tumor, immune-modulating, anti-diabetic, and anti-viral activities as well as radio-protection (Zhu, Du, Bian, & Xu, 2015). Besides, YG has been reported to adsorb mycotoxins and metal ions (Shetty & Jespersen, 2006). YG showed good affinity to mycotoxins, so as to adsorb and bind zearalenone and other toxins (Yiannikouris et al., 2004, 2006).

So far, there has been no report available on the adsorption of fishy odor by YG. Therefore, the aim of this study is to establish the adsorption thermodynamics and kinetics of YG for off-odor compounds (hexanal, 1-octen-3-ol and nonanal) and to elucidate the effect of YG on the release of off-odor compounds in silver carp mince. Both the pseudo-first-order and pseudo-second-order models were used to evaluate the kinetics of the adsorption process. Three isothermal models (Langmuir, Freundlich, and Redlich-Peterson models) were applied to obtain the quantitative thermodynamic parameters for the description of adsorption behaviors.

## 2. Materials and methods

### 2.1. Materials

Yeast β-glucan (YG) was provided by Angel Yeast Co., Ltd (Yichang, Hubei, China), and it was washed with hot water at 100 °C to remove the characteristic odor components of YG before experiment. Fresh silver carp (*Hypophthalmichthys molitrix*) was purchased from Huazhong Agricultural University market in Wuhan, Hubei, China, and transported to the laboratory alive. All the standard compounds were of chromatographic grade: hexanal (≥99%) was purchased from Aladdin Co., Ltd (Shanghai, China); 1-octen-3-ol (> 98%) and nonanal (> 95%) were provided by Shanghai Yuanye Biotechnology Co., Ltd (Shanghai, China); 1, 2-dichlorobenzene (200 μg/mL in methanol) was from Sigma-Aldrich Co., Ltd (Shanghai, China); and methanol (≥99.8%) was provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other chemicals used were of analytical grade.

### 2.2. Morphology of YG by scanning electron microscopy (SEM)

The original and hot water-washed YG samples were sputtered with platinum using an ion sputter coater (MC1000, Kunshan Research Precision Instrument Co., Ltd, Jiangsu, China). The samples were observed and photographed by a scanning electron microscope (JSM-5510LV, JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 20 kV.

### 2.3. Adsorption kinetics of YG for off-odor compounds

On the basis of previous report, hexanal, nonanal, 1-octene-3-ol, 2,4-decadienal, 1-penten-3-ol, 2-undecanone, etc., were considered the contributors to the off-odor of aquatic products (Chen et al., 2016; Fu et al., 2009; Mahmoud & Buettner, 2016b; Varlet, Knockaert, Prost, & Serot, 2006; Yarnpakdee et al., 2012). Our preliminary experiment indicated that nonanal had the highest odor activity value (OAV) in all the investigated off-odor compounds, and it was considered the most important contributor to the fishy odor in silver carp mince, that 1-octen-3-ol had the second highest OAV, and that hexanal showed the highest concentration in silver carp mince. Therefore, this study adopted nonanal, 1-octen-3-ol, and hexanal to conduct YG adsorption experiment.

Adsorption experiments were performed according to the previously reported method with modification (Bayramoglu, Altintas, & Arica, 2009). Three off-odor compounds were completely dissolved in a small amount of methanol, and then were diluted with deionized water to prepare the off-odor solutions. The hot water-washed YG (0.1 g) was added to 100 mL of off-odor solution (hexanal, 10 μg/mL; 1-octen-3-ol, 5 μg/mL; nonanal, 1 μg/mL) in stoppered bottles, and then these stoppered bottles were placed in a magnetic stirring apparatus (DF-101S, Zhengzhou Great Wall Industry and Trade Co., Ltd, Henan, China) at pH of 7 and 37 °C with a low speed of 100 rpm. An aliquot sample solution (6.0 mL) was taken out at intervals (10, 20, 30, 60, and 120 min) and was filtered using 0.45 μm membrane filter. The amount of off-odor compounds in filtrate (5.0 mL) was determined by SPME-GC analysis. The amount of off-odor compounds adsorbed was expressed as $q_t$ (μg/mg) at time t and it was calculated using the following equation:

$$q_t = \frac{(c_0 - c_t)V}{W} \quad (1)$$

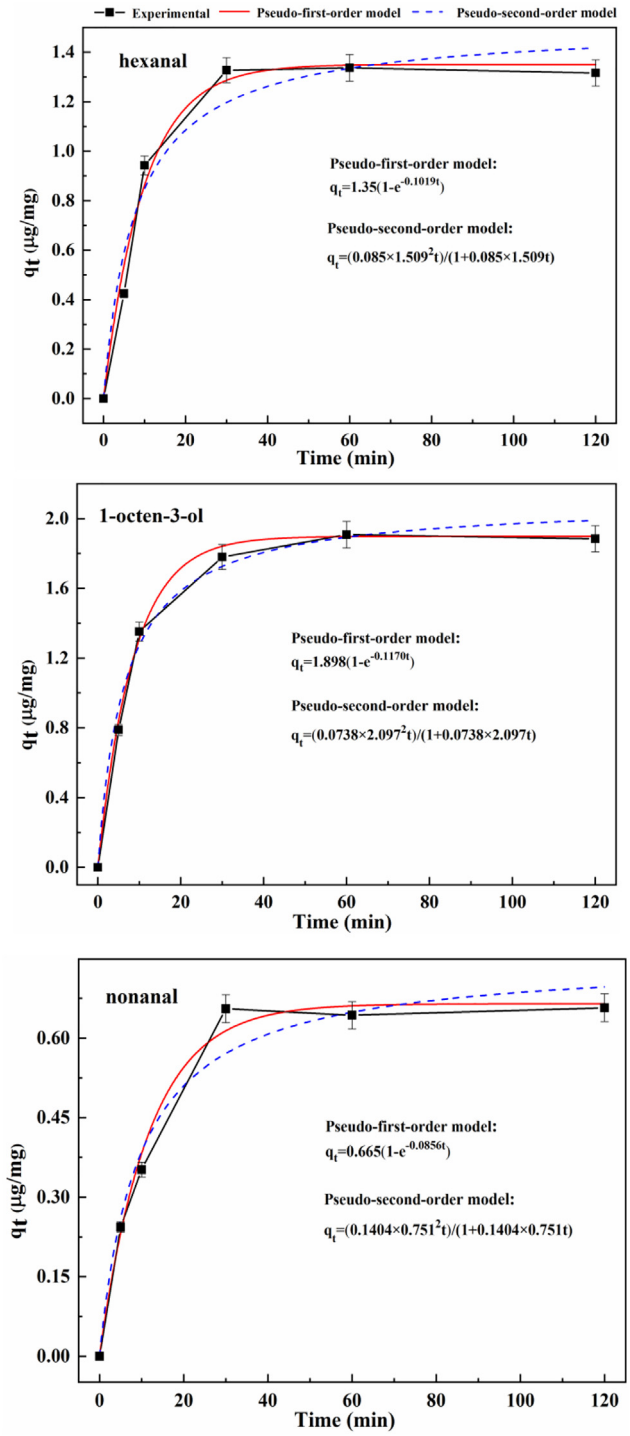


**Fig. 2.** Adsorption kinetics curves of YG for hexanal, 1-octen-3-ol and nonanal.

**Table 1**
Kinetic parameters for the adsorption of YG for hexanal, 1-octen-3-ol and nonanal.

| | $q_{e,exp}$ (μg/mg) | Pseudo-first-order | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|---|
| | | $q_{e,cal}$ (μg/mg) | $k_1$ | $R^2$ | $q_{e,cal}$ (μg/mg) | $k_2$ | $R^2$ |
| Hexanal | 1.316 | 1.350 | 0.1019 | 0.9825 | 1.509 | 0.0850 | 0.9501 |
| 1-Octen-3-ol | 1.884 | 1.898 | 0.1170 | 0.9966 | 2.097 | 0.0738 | 0.9846 |
| Nonanal | 0.657 | 0.665 | 0.0856 | 0.9894 | 0.751 | 0.1404 | 0.9662 |

where $c_0$ and $c_t$ (μg/mL) are the off-odor compounds concentrations of the solution at initial time and at time t, respectively; V (mL) is the volume of the solution; W (mg) is the weight of the hot water-washed YG.

### 2.4. Adsorption isotherms and adsorption thermodynamics of YG for off-odor compounds

Adsorption isotherms and thermodynamic parameters were determined according to the following procedures (Duran, Ozdes, Gundogdu, & Senturk, 2011). YG (0.01 g) were added into the off-odor solution with different concentrations (hexanal and 1-octen-3-ol, 0–10 μg/mL; nonanal, 0–5 μg/mL), and then the off-odor solution added with YG was stirred at 100 rpm for 80 min at 4 °C and 37 °C, respectively. The amount of the adsorbate at equilibrium was expressed as $q_e$ (μg/mg) and it was calculated using the following equation:

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (2)$$

where $c_0$ and $c_e$ (μg/mL) are the initial and equilibrium concentrations of off-odor compounds in the solution, respectively; V is the volume of the solution (mL); W (mg) is the weight of the hot water-washed YG.

### 2.5. Solid phase microextraction – gas chromatography (SPME-GC) analysis of off-odor compounds

Off-odor compounds were quantified by SPME-GC according to the previously reported method with modification (Selli et al., 2009). The as-prepared solution (5.0 mL) was transferred into a headspace vial for sealing. The sample vial was closely capped with a PTFE-silicon stopper and equilibrated at 60 °C for 3 min. Then, the 50/30 μm DVB/CAR/PDMS fiber (Supelco, Inc, Bellefonte, USA) of SPME was inserted into the headspace with continuous heating and agitation (250 rpm) for 20 min. After extraction, the fiber was put into the injection port of GC and desorbed at 250 °C for 5 min.

GC analysis was performed on an Agilent 6890 GC system (Agilent Inc., Palo Alto, California, USA) with a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). A flame ionization detector (FID) was used to quantify the off-odor compounds. Oven temperature was held for 5 min at 40 °C, then, it increased to 105 °C at 6 °C/min and then to 220 °C at 25 °C/min, and finally the temperature was held for 3 min. The FID and injector temperatures were set as 250 °C. The gas flow rate of nitrogen (carrier gas) was 25 mL/min; that of hydrogen was 30 mL/min, and that of air was 400 mL/min. The standards of three off-odor compounds were quantified in GC system to establish their external standard curves of peak area vs. concentration.

### 2.6. Preparation of silver carp mince added with YG

Each of fresh silver carp weighing ~1.5 kg was immediately beheaded, descaled, eviscerated, and washed with tap water. The white muscle was only collected and minced in a mixer (HR7625, Hong Kong Philips Domestic Appliance Co., Ltd, Hong Kong, China) for 2 min. Then, 2% hot water-washed YG (based on mass of silver carp mince) were added into silver carp mince, all which were chopped for another 2 min. The silver carp mince with and without YG (control) were stored at 4 °C before SPME-GC–MS analysis.

### 2.7. SPME-GC–MS analysis of off-odor compounds in silver carp mince added with YG

The silver carp mince (3 g) with or without YG samples and the internal standard (300 μL of 1 μg/mL 1,2-dichlorobenzene) were immediately transferred into a 20 mL headspace vial containing 7 mL of NaCl saturated solution. The sample vial was closely capped with a PTFE-silicon stopper, followed by the equilibration at 60 °C for 3 min.

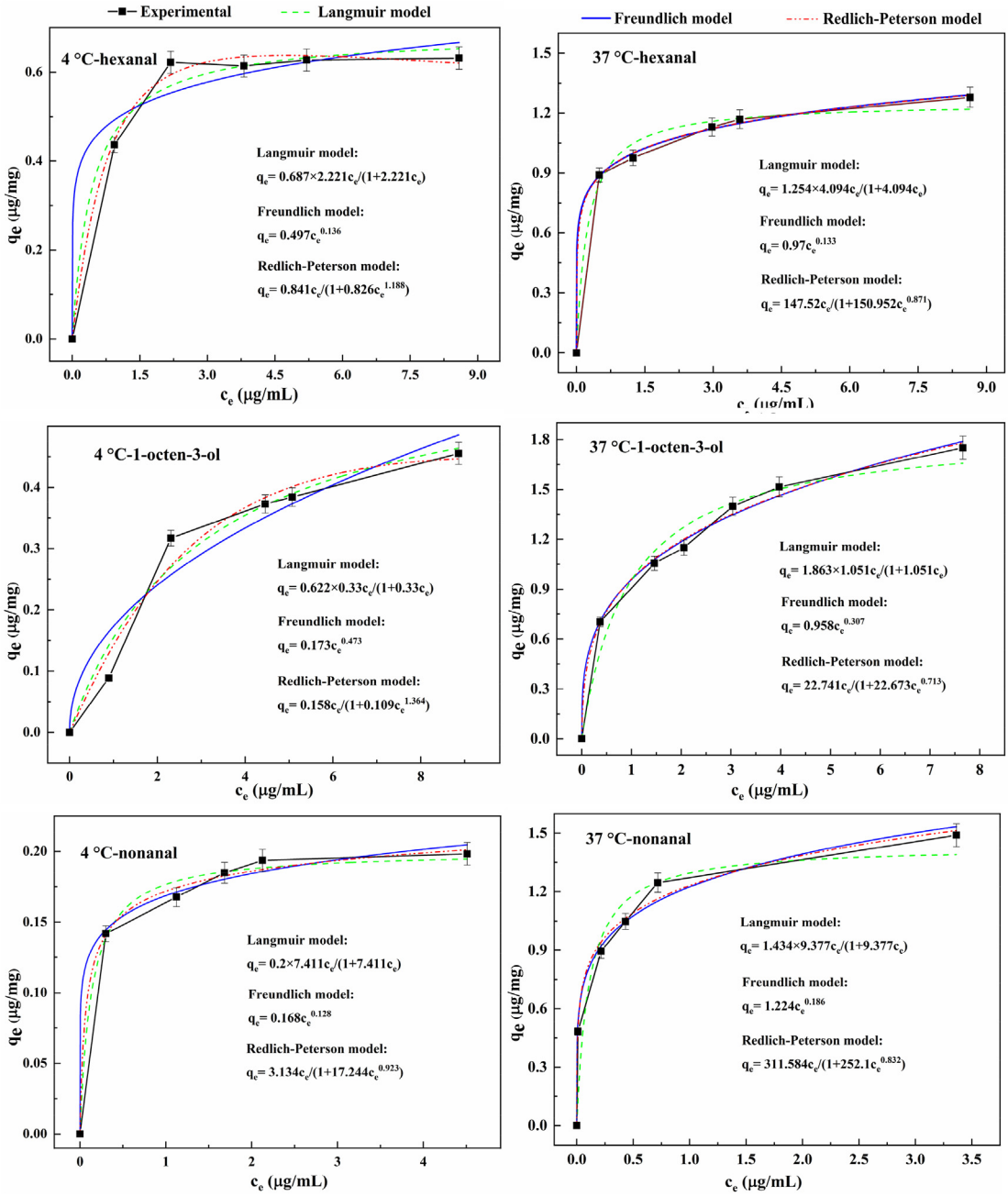


**Fig. 3.** Adsorption isotherm of YG for hexanal, 1-octen-3-ol and nonanal at different temperatures.

**Table 2A**
Isotherm parameters for the adsorption of YG for hexanal, 1-octen-3-ol and nonanal.

| | T (°C) | Langmuir | | | Freundlich | | | Redlich–Peterson | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $q_m$ (μg/mg) | $K_L$ | $R^2$ | $K_F$ | 1/n | $R^2$ | A | B | g | $R^2$ |
| Hexanal | 4 | 0.687 | 2.221 | 0.9842 | 0.497 | 0.14 | 0.9622 | 0.841 | 0.826 | 1.188 | 0.9920 |
| | 37 | 1.254 | 4.094 | 0.9863 | 0.970 | 0.13 | 0.9987 | 147.520 | 150.952 | 0.871 | 0.9982 |
| 1-Octen-3-ol | 4 | 0.622 | 0.330 | 0.9610 | 0.173 | 0.47 | 0.9189 | 0.158 | 0.109 | 1.364 | 0.9587 |
| | 37 | 1.863 | 1.051 | 0.9629 | 0.958 | 0.31 | 0.9945 | 22.741 | 22.673 | 0.713 | 0.9934 |
| Nonanal | 4 | 0.200 | 7.411 | 0.9919 | 0.168 | 0.13 | 0.9937 | 3.134 | 17.244 | 0.923 | 0.9940 |
| | 37 | 1.434 | 9.377 | 0.8667 | 1.224 | 0.19 | 0.9890 | 311.584 | 252.100 | 0.832 | 0.9886 |

**Table 2B**
Thermodynamic parameters for the adsorption of YG for hexanal, 1-octen-3-ol and nonanal.

| | T (°C) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/K mol) |
|---|---|---|---|---|
| Hexanal | 4 | −1.839 | 16.92 | 54.42 |
| | 37 | −3.635 | | |
| 1-Octen-3-ol | 4 | 2.555 | 25.32 | 81.21 |
| | 37 | −0.128 | | |
| Nonanal | 4 | −4.615 | 14.33 | 35.06 |
| | 37 | −5.772 | | |

Then, the 50/30 μm DVB/CAR/PDMS fiber (Supelco Inc, Bellefonte, USA) of solid phase microextraction (SPME) was inserted into the headspace with continuous heating and agitation (250 rpm) for 50 min. After extraction, it was put into the injection port of GC–MS and desorbed at 250 °C for 5 min.

Agilent 7890 GC-5977 MS (Agilent Inc., Palo Alto, CA, USA) equipment matching with a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm) was employed for separating and identifying the volatile compounds of the samples. Temperature programme and GC–MS conditions were set as recently reported by Mahmoud and Buettner (2016a) with modification. The oven program was as follows: initial temperature 40 °C (held for 3 min), then rose to 200 °C at 5 °C/min (held for 2 min), and finally reaching 250 °C at 50 °C/min (held for 5 min). Helium was used as the carrier gas at a flow rate of 1.0 mL/min with the splitless GC inlet mode. The MS fragmentation was performed by electronic impact (EI) mode (ionization energy, 70 eV; source temperature, 230 °C). The transmission line and quadrupole temperature was 280 °C and 150 °C, respectively. The acquisition mode was full-scan with mass acquisition range of 35–550 *m/z*.

The estimated concentration $c_i$ (μg/kg) of each volatile compound in the sample was calculated using the following equation:

$$c_i = \frac{A_i W_{is}}{A_{is} W} \quad (3)$$

where $A_i$ and $A_{is}$ are peak area of a volatile compound and internal standard in the GC, respectively; $W_{is}$ (μg) and W (kg) are the weight of the internal standard and sample, respectively.

### 2.8. Statistical analysis

All experiments were performed in triplicate and repeated in three batches of samples. The data were analyzed and fitted by nonlinear regression model using Origin 9.0 (Origin Lab Inc., Northampton, MA, USA), and the results were expressed as mean values ± SD (standard deviation). Statistically significant difference was defined at $p < 0.05$ by using analysis of variance (ANOVA) and Duncan's multiple range tests by SPSS22.0 software (SPSS Inc., Chicago, IL, USA).

## 3. Results and discussion

### 3.1. Characteristic of the YG surface

SEM was employed to observe the microscopic structure including the macro-pore size and distribution. Fig. 1 shows SEM photographs of the untreated (A and B) and hot water-treated (C and D) YG. In general, the two analyzed samples were similar in the morphology with a porous appearance and visible traces of cell wall structure (Fig. 1B and D). However, significant differences in the particle size and distribution were observed between these two samples (Fig. 1A and C). The untreated YG presented a larger and rounder cluster (Fig. 1A), while hot water-treated YG had a smaller particle size with an irregular and fragmented structure (Fig. 1C). Furthermore, the hot water-treated sample (Fig. 1D) showed a more porous and spongy structure than the untreated sample (Fig. 1B). Our finding was consistent with the previous reports that the treatment process, such as heating and drying, resulted in the difference in microstructure (Limberger-Bayer et al., 2014). Besides, another study reported that the powdered activated carbon with more tiny pores could reduce fishy odor without changing physiochemical and functional properties of tiger puffer (*Takifugu rubripes*) skin gelatin (Pan et al., 2018). Therefore, it could be speculated that the treated YG with the more porous and spongy structure was suitable for the adsorption of volatile compounds. Additionally, the insolubility of YG led to the formation of three-dimensional structure that was identified as the most favorable structure for adsorption process (Yiannikouris et al., 2004).

### 3.2. Adsorption kinetics and adsorption capacities of YG for off-odor compounds

Adsorption kinetics describes the adsorption rate of the adsorbate on an adsorbent and the adsorption time from the beginning to equilibrium. Fig. 2 shows the adsorption kinetics curves of YG for hexanal, 1-octen-3-ol and nonanal at 37 °C. The adsorption capacities of YG for three off-odor compounds increased with the prolongation of contact time. The adsorption increased rapidly at the first 30 min and then increased slowly until equilibrium.

In order to elucidate the adsorption mechanisms of YG for hexanal, 1-octen-3-ol, and nonanal, the pseudo-first-order and pseudo-second-order kinetics models were used to fit the experimental data and to evaluate the adsorption processes (Aziz & Kim, 2017). The two models can be expressed as follows:

Pseudo-first-order model:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

Pseudo-second-order model:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where $q_t$ (μg/mg) is the amount of adsorbed off-odor compounds at time t; $q_e$ (μg/mg) is the adsorption capacity of off-odor compound at

**Table 3**
Effect of YG on characteristic volatile compounds in white meat of silver carp.

| Characteristic volatile compounds | Odor threshold (μg/kg) | Mince | | Mince/YG | | Odor description |
|---|---|---|---|---|---|---|
| | | Concentration (μg/kg) | OAV | Concentration (μg/kg) | OAV | |
| Hexanal | 5 | 487 ± 23[a] | 97 ± 5 | 375 ± 44[b] | 75 ± 9 | Fishy, Grassy |
| Nonanal | 1.1 | 319 ± 31[a] | 290 ± 28 | 241 ± 21[b] | 219 ± 19 | Green, fatty |
| Decanal | 2 | 53 ± 13[a] | 26 ± 7 | 50 ± 10[a] | 25 ± 5 | Citrussy |
| 2-Octenal | 3 | 24 ± 7[a] | 8 ± 2 | 15 ± 3[a] | 5 ± 1 | Fishy |
| 2,4-Decadienal | 0.07 | 7 ± 3[a] | 105 ± 36 | 5 ± 1[a] | 67 ± 7 | Fatty, green |
| 1-Octen-3-ol | 1.5 | 184 ± 26[a] | 123 ± 17 | 129 ± 23[b] | 86 ± 15 | Mushroom-like |

Different lowercase letters in the same row indicate significant difference ($p < 0.05$).

equilibrium per unit of YG; $k_1$ and $k_2$ are the rate constant of the pseudo-first and pseudo-second-order models, respectively.

The pseudo-first order model is generally applicable over the initial stage of adsorption process, while the pseudo-second-order model predicts the entire adsorption process that is mainly characterized by chemisorption (Chang et al., 2012). After the experimental data fitted by the two kinetic models, the kinetic parameters of YG adsorption for hexanal, 1-octen-3-ol and nonanal were obtained and shown in Table 1. The $R^2$ for the pseudo-first-order kinetic model (0.9825–0.9966) was higher than that of the pseudo-second-order kinetic model (0.9504–0.9846), implying the pseudo-first-order kinetics model was a more suitable model for exhibiting the adsorption processes of YG than the pseudo-second-order model. Our experimental results indicated that adsorption capacities ($q_e$) of YG for hexanal, 1-octen-3-ol and nonanal were 1.316, 1.884, and 0.657 μg/mg, respectively. In comparison, the theoretical adsorption capacities of YG for hexanal, 1-octen-3-ol, and nonanal were calculated to be 1.350, 1.898 and 0.665 μg/mg, respectively, based on the pseudo-first-order kinetics model. The calculated values matched well with the experimental results. Hence, the pseudo-first-order kinetics model was fitted for evaluating the adsorption behaviors of YG for three off-odor compounds. It was worth noting that the adsorption capacity of YG for hexanal and 1-octen-3-ol was much higher than for nonanal, which might be attributed to the fact that nonanal had a long chain, resulting in steric hindrance to affect its binding affinity to YG (Gianelli, Flores, & Toldrá, 2003).

### 3.3. Adsorption isotherms of YG for off-odor compounds

Adsorption isotherms describe the relationship between the adsorption capacity of adsorbent and the equilibrium concentration of adsorbate in liquid when the adsorption achieves equilibrium at a given temperature (Bayramoglu et al., 2009). Fig. 3 shows the adsorption isotherms of YG for hexanal, 1-octen-3-ol and nonanal at 4 °C and 37 °C. The equilibrium adsorption capacity ($q_e$) for three off-odor compounds at 37 °C was higher than that at 4 °C, suggesting that the adsorption processes of YG for three off-compounds were endothermic in natural environment, which was verified by our subsequent thermodynamic studies. Additionally, the adsorption capacity of YG for hexanal, 1-octen-3-ol and nonanal increased rapidly at low concentration, but it increased slowly at high concentration. Therefore, the initial off-odor compound concentration and temperature played important roles in the adsorption process. As reported in previous studies, the adsorption capacity was influenced by the number of binding sites and environmental conditions (Limousin et al., 2007).

The adsorption behavior and mechanism were further investigated by fitting the data using Langmuir, Freundlich, and Redlich-Peterson models. These three models are most frequently used to develop isotherms for different adsorbent/adsorbate systems and to explain solid-liquid adsorption and predict their equilibrium parameters (Wang et al., 2013). The three isotherm models were expressed as the following equations:

Langmuir isotherm model:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{6}$$

Freundlich isotherm model:

$$q_e = K_F {c_e}^{1/n} \tag{7}$$

Redlich-Peterson isotherm model:

$$q_e = \frac{A c_e}{1 + B {c_e}^g} \tag{8}$$

where $q_e$ (μg/mg) is the adsorption capacity at equilibrium; $c_e$ (μg/mL) is the equilibrium concentration of off-odor compounds in solution; $q_m$ (μg/mg) is the maximum adsorption capacity; $K_L$ and $K_F$ are the Langmuir constant and Freundlich constant; 1/n is the adsorption intensity; A and B are the Redlich-Poetersn isotherm constants, and g is the Redlich-Peterson isotherm exponent ranging from 0 to 1.

The resultant adsorption parameters for three isotherms are presented in Table 2A. Except for nonanal at 37 °C and 1-octen-3-ol at 4 °C, the correlation coefficient ($R^2$) was within a range of 0.9587–0.9982, indicating that Langmuir, Freundlich, and Redlich-Peterson models were suitable for fitting the isotherm adsorption data of YG for hexanal, 1-octen-3-ol, and nonanal. Langmuir model assumes that the adsorption occurs on a homogeneous surface by monolayer adsorption without any interaction between adjacent adsorbed molecules due to a finite number of identical sites on the surface of adsorbent (Sandhu & Gu, 2013). For Langmuir equation, $K_L$ is an important parameter related to the affinity of the binding sites. The $K_L$ value at 37 °C was higher than that at 4 °C, implying that a higher affinity at 37 °C than at 4 °C. The $R^2$ values of the Langmuir equation for nonanal at 37 °C was lower than for other off-odor compounds. It suggested that the adsorption of YG for nonanal might not be a monolayer adsorption, and that the space steric hindrance of nonanal molecules might result in the repulsive interactions between adjacent nonanal molecules. Freundlich isotherm model describes the heterogeneous surface energies by multilayer adsorption (Duran et al., 2011). The constants $K_F$ and 1/n are indicators of the adsorption capacity and intensity of YG for off-odor compounds, respectively (Bayramoglu et al., 2009). When $0.1 < 1/n \leq 0.5$, adsorption is strong; $0.5 < 1/n \leq 1$, it is easy to adsorb; $1/n > 1$, it is difficult to adsorb (Samiey & Dargahi, 2010). Tables 2A an 2B shows that the values of 1/n ranged from 0.13 to 0.47, indicating that the adsorption of YG for three off-odor compounds were strong at both selected temperature. Moreover, the 1/n values of hexanal and nonanal were much lower than those of 1-octen-3-ol, suggesting that the adsorption of YG for hexanal and nonanal could occur more easily than for 1-octen-3-ol. Redlich-Peterson isotherm is an intermediate isotherm model that combines the features of both Langmuir and Freundlich isotherms. Therefore, it can be applied to either homogeneous or heterogeneous system (Foo & Hameed, 2010). Redlich-Peterson isotherm becomes a special case of Langmuir, when Redlich-Peterson isotherm constant g is set as 1 (Wang et al., 2013). In this study, Redlich-Peterson equation provided the best fitting in most cases, and the g values were located within the range of 0–1, except the g values of hexanal and 1-octen-3-ol at 4 °C were slightly beyond 1. Moreover, the g values were close to 1, implying that these isotherms conformed to Langmuir model better than to Freundlich one.

### 3.4. Adsorption thermodynamics of YG for off-odor compounds

Adsorption thermodynamics gains an insight into the adsorption process and reveals the adsorption mechanism. The thermodynamic parameters including the change in enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) were calculated by the Van't Hoff equation and the tenth equation (Liu, Ying, Sanguansri, & Augustin, 2019):

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

$$\Delta G^\circ = -RT\ln K_L \tag{10}$$

where R is the gas constant (8.314 J $mol^{-1}$ $K^{-1}$); T is the absolute temperature (K); $K_L$ is the Langmuir constant (Liu, 2009).

Table 2B presents the thermodynamic parameters (ΔG°, ΔH° and ΔS°) of the adsorption of YG for hexanal, 1-octen-3-ol and nonanal at different temperatures. For all the 3 off-odor compounds, the values of ΔG° at 37 °C was lower than those at 4 °C, indicating that the adsorption process was more favorable at high temperature than at low temperature and belonged to a endothermic process. Moreover, all ΔG° values were found to be negative at 37 °C, suggesting that the adsorption of YG for three off-odor compounds were all spontaneous and thermodynamically feasible (Yousef, El-Eswed, & Al-Muhtaseb, 2011). The ΔH° value of YG adsorption for hexanal, 1-octen-3-ol and nonanal were

16.92, 25.32, and 14.33 kJ/mol, respectively. The positive value of $\Delta H^{\circ}$ demonstrated endothermic nature of YG for hexanal, 1-octen-3-ol and nonanal (Liu et al., 2019). Meanwhile, all the values of $\Delta H^{\circ}$ were < 40 kJ/mol, indicating that physical adsorption was the dominant mechanism in the entire adsorption process (Gao, Yu, Yue, & Quek, 2013). Additionally, the positive values of $\Delta S^{\circ}$ suggested the high affinity of hexanal, 1-octen-3-ol and nonanal towards the YG to increase randomness at the solid-solution interface (Sun et al., 2008).

The thermodynamic parameters provided the main evidence for confirming interaction forces between YG and organic small molecules, and the acting forces included hydrophobic force, electrostatic force, Van der Waals interactions, hydrogen bonds, etc (Hu, Yu, Dong, Yang, & Liu, 2006). When $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$, interaction forces were mainly hydrophobic interactions; when $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} < 0$, interaction forces mainly included Van der Waals interactions and hydrogen bonds; when $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} > 0$, there were mainly electrostatic interactions (Li, Zhu, Jin, & Yao, 2007). In this study, the values of $\Delta H^{\circ}$ and $\Delta S^{\circ}$ were positive, indicating that the interaction between YG and three off-odor compounds was mainly hydrophobic interactions.

### 3.5. Effect of YG on off-odor compounds in silver carp mince

The effect of YG on the active off-odor compounds in silver carp mince is presented in Table 3. The contribution of each volatile compound was described by OAV, which could be obtained from dividing the concentration of the compound by its odor threshold (Frauendorfer & Schieberle, 2006). When OAV was greater than or equal to 1, the compound was defined as an active volatile compound, and it contributed to the overall aroma profile of sample. As indicated in Table 3, the OAVs of 6 off-odor compounds were more than 1, i.e., hexanal, nonanal, decanal, 2-octenal, 2, 4-decadienal, and 1-octen-3-ol. Therefore, these 6 compounds were defined as fishy odor-active compounds, and they played important roles in determining the integral off-odor characteristics of silver carp.

Among the aldehydes, hexanal showed the highest concentration (486.94 μg/kg) in fish mince. Hexanal was mainly generated from the oxidative degradation of lipid acids (linoleate and linolenate), and it contributed the fishy odor to fish meat samples (Maqsood & Benjakul, 2011). Selli et al. (2009) identified nonanal and (*E*,*E*)-2,4-octadienal as the most important contributors to the overall odor of rainbow trout fish. Varlet et al. (2006) also found nonanal, 2-octanal, decanal, and 2, 4-decadienal were responsible for fishy odor in fish products. Our study found that nonanal had the highest OAV of 289.63, and that it generated a lipid-oxidized odor and it was the most important contributor to the fishy odor in the silver carp mince. Our study also found that 1-octen-3-ol exhibited the second highest OAV of 122.54. This compound was widely reported to have a mushroom-like odor, and it might be generated from saturated fatty acids Samiey, by enzyme-catalyzed β-oxidation (Giri, Osako, & Ohshima, 2010). Based on these findings, it could be inferred that 1-octen-3-ol might be responsible for unpleasant odor characteristics of fish products.

Interestingly, with the addition of YG to the fish mince, the contents of 6 fishy odor-active compounds displayed a decrease at different levels. In particular, the contents of hexanal, nonanal and 1-octen-3-ol in fish mince/YG complex decreased by 22.9%, 24.5% and 29.9% ($p < 0.05$), respectively, in contrast to that of single fish mince. This result could be explained by the fact that these 3 fishy odor compounds were adsorbed and bound to the YG from silver carp mince. The addition of YG enhanced the binding capability between the off-odor compounds and the YG macromolecules, thus reducing the release of off-odor compounds.

## 4. Conclusions

In this work, the adsorption thermodynamics and kinetics characteristics of YG for 3 off-odor compounds (hexanal, 1-octen-3-ol, nonanal) were investigated. The kinetic experiments indicated that the pseudo-first-order kinetic model was a better model to describe the adsorption processes of YG for 3 off-odor compounds, and that the adsorption capacity of YG for hexanal and 1-octen-3-ol were much higher than for nonanal. Moreover, Langmuir, Freundlich and Redlich-Peterson isotherm models were applied to predict the relevant isotherm parameters, and these 3 models fitted well the isotherm adsorption data of YG for hexanal, 1-octen-3-ol and nonanal. Thermodynamic studies demonstrated that the adsorption was endothermic, spontaneous, and thermodynamically feasible, and that the adsorption mechanism was mainly dominated by physical adsorption and hydrophobic interaction. Additionally, the contents of hexanal, 1-octen-3-ol, and nonanal released from mince/YG complex decreased by 22.8%, 29.9%, and 24.5% ($p < 0.05$), respectively, in contrast to those from mince without additional YG. Therefore, this work reveals that YG could adsorb the off-odor compounds and reduce their release from the silver carp mince. Our findings provide a new method for the deodorization of fish products.

## Author contributions

This study was designed by QL Huang. Sample preparation and experiments were performed by HM Zhang. Data analysis was conducted by HM Zhang, D Wu, ZY Liu, XG Luo, SB Xiong, T Yin. Original draft was written by HM Zhang and QL Huang. Authors D Wu and QL Huang revised the manuscript and improved the language. All the authors read and approved the final manuscript.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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