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Powdered activated carbon adsorption of two fishy odorants in water: Trans,trans-2,4-heptadienal and trans,trans-2,4-decadienal

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ABSTRACT

Powdered activated carbon (PAC) adsorption of two fishy odorants, trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE), was investigated. Both the pseudo first-order and the pseudo second-order kinetic models well described the kinetics curves, and DDE was more readily removed by PAC. In isotherm tests, both Freundlich and Modified Freundlich isotherms fitted the experimental data well. PAC exhibited a higher adsorption capacity for DDE than for HDE, which could be ascribed to the difference in their hydrophobicity. The calculated thermodynamic parameters (ΔG^0, ΔH^0, and ΔS^0) indicated an exothermic and spontaneous adsorption process. PAC dosage, pH, and natural organic matter (NOM) presence were found to influence the adsorption process. With increasing PAC dosage, the pseudo first-order and pseudo second-order rate constants both increased. The value of pH had little influence on HDE or DDE molecules but altered the surface charge of PAC, and the maximum adsorption capacity occurred at pH 9. The presence of NOM, especially the fraction with molecular weight less than 1 k Dalton, hindered the adsorption. The study showed that preloaded NOM impaired the adsorption capacity of HDE or DDE more severely than simultaneously fed NOM did.

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Introduction

The presence of taste and odor (T&O) compounds in drinking water is a common and recurrent problem for many utilities, since palatability is often consumers' only direct indication of the safety of drinking water (Watson, 2004; Satchwill et al., 2007), and a negative perception can in many cases spark mistrust toward the industry (Zhang et al., 2010, 2011). In the last few decades, T&O episodes have been reported in many places, such as the Glenmore Reservoir in Canada (Watson et al., 2001), Lake Winnebago in the United States (Young et al., 1999), Lake Zurich and Lake Greifensee in Switzerland (Peter et al., 2009), and Taihu Lake in China (Yang et al., 2008). Thus,

it is of great importance to develop effective measures to mitigate the off-flavor in drinking water.

Ever since geosmin was found in drinking water (Gerber and Lechevalier, 1965), many odorous chemicals were confirmed to be sources of T&O events (Wnorowski, 1992; Suffet et al., 1996, 1999). Among those odorants, a major part could be attributed to microbial metabolism (Suffet et al., 1999; Hockelmann and Jüttner, 2005). Although the two prevalent earthy–musty odorants i.e., geosmin and 2-methylisoborneol have been extensively discussed, research on other off-flavor compounds has been relatively scarce.

Trans,trans-2,4-heptadienal (HDE, $C_7H_{10}O$) is reported to be an unsaturated fatty acid derived from chrysophytes (Yano et al., 1988;

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Watson and Satchwill, 2003). It could contribute a severe rancid or fishy odor to water (Khiari et al., 1995). On the other hand, trans,trans-2,4-decadienal (DDE, $C_{10}H_{16}O$) is a lipooxygenase-mediated cleavage product of diatoms (Miralto et al., 1999; Jüttner, 2001) or chrysophytes (Jüttner, 1995). It renders the drinking water fishy or oily (Watson, 2004). Physical and chemical properties of the two compounds are as follows: molecular weight are 110.15, 152.23; boiling points are 177.4 and 244.6°C; $logK_{OW}$ are 2.11 and 3.18, for HDE and DDE, respectively, while OTC for HDE is 2.5–5 μg/L, and 0.07 μg/L for DDE.

The two odorants have been found in natural water bodies and a few publications have discussed mitigation methods. Watson et al. (2001) concluded that chlorination had little effect on HDE. Jo (2008) found that UV/H_2O_2 was effective in eliminating HDE and DDE. However, this advanced oxidation process is costly and not practical for drinking water treatment plants. Powdered activated carbon (PAC) adsorption has been proved to be an effective method in dealing with various pollutants as well as T&O compounds in water (Kim et al., 1997; Tan et al., 2008). As far as the authors know, the application of PAC adsorption to HDE and DDE has not been previously reported.

In this study, our objective is to investigate the characteristics and mechanisms of PAC adsorption of HDE and DDE, including kinetics, equilibria, and thermodynamic studies. In addition, the effects of PAC dosage, pH, and natural organic matter (NOM) were also studied.

1. Materials and methods

1.1. Chemicals

HDE (90%) was purchased from Sigma-Aldrich (USA) and DDE (95%) was obtained from Acros Organics (Belgium). NaCl was bought from Sigma-Aldrich and heated at 450°C for 4 hr before use. Stock solutions of HDE and DDE were prepared in methanol (HPLC-grade, J.T. Baker, Center Valley, PA, USA). All other solutions were prepared using water from a Milli-Q ultrapure water purification system.

Properties of the PAC used (F-400, Calgon Carbon Co., China) are as follows: ash content <5.81%, specific area 1087 m²/g, average pore size 2.42 nm, pore volume 0.63 mL/g, iodine number 1071 mg/g, methylene blue adsorption 225 mg/g, the pore size distribution for <2.0 nm, 2.0–3.0 nm, 3.0–5.0 nm, 5.0–10.0 nm, 10.0–20.0 nm, and >20.0 nm are 64.34%, 7.77%, 13.06%, 8.60%, 5.76%, and 0.47%, respectively. Prior to use, PAC was dried for 5 hr at 105°C.

1.2. Chemical analysis

Concentrations of HDE and DDE were analyzed using liquid phase chromatography with an ultraviolet detector. The 1260 infinity high performance liquid chromatography system (Agilent Technologies, Santa Clara, CA, USA) was used for odorant detection with an Eclipse Plus C-18 column (Agilent Technologies, Santa Clara, CA, USA). The mobile phase consisted of 95:5 H_2O:acetonitrile for HDE and 100% acetonitrile for DDE, and the flow rate was 0.5 mL/min. The UV absorbance peak occurred at 281 nm and 282 nm for HDE and DDE respectively.

In NOM effect experiments, the quantification of off-flavor compounds was achieved by headspace solid phase micro-extraction (HS-SPME) coupled with gas chromatography/mass spectrometry (GC/MS). The GC Sampler 80 (Agilent Technologies, Santa Clara, CA, USA) was utilized in the automated HS-SPME process. A 7890A gas chromatograph attached to a 5975C mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) was employed to analyze the odorants. The column used was an HP-5MS 30 m × 0.25 mm × 0.25 μm (Agilent Technologies, Santa Clara, CA, USA). Divinylbenzene/carboxen/poly-dimethylsiloxane stableflex (DVB/CAR/PDMS) SPME fiber (Agilent Technologies, Santa Clara, CA, USA) was used for sample preconcentration and was conditioned according to manufacturer instruction at 270°C for 1 hr. High purity helium, delivered at a constant flow of 1 mL/min, was used as carrier gas. The mass spectrometer was used in EI mode (70 eV) with 5 min solvent delay.

1.3. Natural organic matter

Humic acid was purchased from Sigma-Aldrich (USA). A certain amount of NOM was mixed with ultrapure water for 24 hr and then the solution was filtered through a 0.45 μm Millipore filter (diameter: 47 mm, Merk Millipore, Billerica, MA, USA). The NOM solution was then fractionated into six nominal molecular weight (MW) fractions: <1000, <3000, <5000, <10000, <30000, and <100000 with ultrafiltration membranes (material: regenerated cellulose, diameter: 76 mm, Merk Millipore, Billerica, MA, USA). The total organic carbon (TOC) contents of the fractions were measured by a TOC-V_{CPH} analyzer (Shimadzu, Kyoto, Japan).

1.4. Determination of point of zero charge of PAC

The determination of point of zero charge (pH_{pzc}) was carried out using the pH titration method (Órfão et al., 2006). Several 200 mL glass bottles were filled with 0.01 mol/L NaCl solution. The pH of the solution within each bottle was adjusted to a value between 2 and 11 by the addition of NaOH or HCl solution. Then, 0.6 g of PAC was added into each bottle and the final pH was measured after 48 hr. The pH_{pzc} is defined as the point where the curve pH_{final} vs. $pH_{initial}$ crosses the line $pH_{final} = pH_{initial}$.

1.5. Procedure

All the tests were carried out on a customized shaker in 600 mL glass bottles containing HDE or DDE solution at 298 K. If needed, solution pH was adjusted to the desired level with phosphate buffer solution, NaOH, or HCl. Since no significant pH variations were observed during the experiments, the initial pH values were perceived to be constant. Adsorption reactions were initiated by the addition of a certain amount of PAC. In kinetics tests, 2 mL samples were collected at designated time intervals. In isotherm experiments, the adsorption process ran for 48 hr to achieve equilibrium. All the thermodynamics tests were the same as the adsorption isotherm tests, except that three additional temperatures, including 308, 318, and 328 K, were tested.

Table 1 – Kinetic and isotherm models used for data analysis.

Models	Equations	Constants	Remarks
Pseudo first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	k_1	k_1 (min^{-1}) is the pseudo first-order rate constant
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	k_2	k_2 (mg/(μg·min)) is the pseudo second-order rate constant
Elovich	$q_t = a + b \log t$	a, b	a (μg/mg) and b are the Elovich model constants
Weber–Morris intraparticle diffusion	$q_t = k_{int} t^{\frac{1}{2}}$	k_{int}	k_{int} (mg/$\left(g \cdot min^{\frac{1}{2}}\right)$) is the intraparticle diffusion rate constant
Freundlich	$q_e = K_f c_e^{\frac{1}{n}}$	K_f, $1/n$	K_f (μg$^{1-(1/n)}$L$^{1/n}$mg^{-1}) and n are the Freundlich isotherm constants, indicating relative adsorption capacity and intensity of adsorption, respectively
Langmuir	$q_e = \frac{b q_m c_e}{1 + b c_e}$	b, q_m	b (L/μg) is the Langmuir isotherm constant related to free energy of adsorption, q_m (μg/mg) is the Langmuir maximum adsorption capacity
Elovich	$\frac{q_e}{q_m} = K_E c_e \exp\left(-\frac{q_e}{q_m}\right)$	K_E, q_m	K_E (L/μg) is the Elovich isotherm constant, q_m (μg/mg) is the Elovich maximum adsorption capacity
Modified Freundlich	$q_e = K'_f \left(\frac{c_e}{D}\right)^{\frac{1}{n'}}$	K'_f, $1/n'$	K'_f (μg$^{1-(1/n')}$mg$^{(1/n')-1}$) and n' are the Freundlich isotherm constants
Temkin	$\theta = \frac{RT}{\Delta Q}\ln(K_0 c_e)$	θ, R, T, ΔQ, K_0	θ ($\theta = q_e/q_m$) is the fraction coverage, R (8.314 J/(mol·K)) is the universal gas constant, T (K) is the temperature, ΔQ (J/mol) is the adsorption energy variation, K_0 (L/μg) is the Temkin isotherm constant

1.6. Data analysis

In the isotherm study, the adsorption capacity or carbon loading at equilibrium, i.e., q_e (μg/mg) was used for model fitting, while in kinetic experiments, the adsorption capacity at time t (min), i.e., q_t (μg/mg) was also calculated. The values of q_t and q_e can be acquired as follows:

$$q_t = \frac{c_0 - c_t}{D} \tag{1}$$

$$q_e = \frac{c_0 - c_e}{D} \tag{2}$$

where, c_0 (μg/L) is the initial concentration of odorant, c_t (μg/L) is the odorant concentration at time t, c_e (μg/L) is the odorant concentration at equilibrium, and D (mg/L) is the PAC dosage.

The experimental data were fitted using different kinetic models (pseudo first-order, pseudo second-order, Elovich, and Weber–Morris intraparticle diffusion models) and equilibrium models (Freundlich, Langmuir, Elovich, Modified Freundlich, and Temkin models). Model equations and constants are listed in Table 1.

2. Results and discussion

2.1. Adsorption kinetics

Theoretically, three steps are involved in the kinetics process (Lazaridis and Asouhidou, 2003): (1) external mass transfer, i.e., the transfer of adsorbate between the bulk fluid and the surface of adsorbent particles; (2) intraparticle diffusion, which is the entrance of adsorbate into adsorbent pores and the diffusion in pores; and (3) mass action at phase boundaries. In physical adsorption, the last step is very rapid and the process is controlled by external mass transfer or intraparticle diffusion (Qiu et al., 2009). Based on these steps, different models have been put forward to describe or predict adsorption kinetics. The measured and modeled adsorption kinetics curves are depicted in Fig. 1 and their kinetic parameters are summarized in Table 2.

Both the pseudo first-order model and the pseudo second-order model appeared to well describe the adsorption curves of the two odorants in terms of correlation coefficient ($r > 0.980$), and DDE exhibited a higher adsorption rate than HDE. Both two models assume that the driving force for adsorption is the difference between the average odorant concentration in solid phase q_t and the equilibrium concentration q_e, and the overall adsorption rate is proportional to either the driving force (as in the pseudo first-order equation) or the square of the driving force (as in the pseudo second-order equation). However, the former mainly simulates rapid adsorption owing to the absence of adsorbent–adsorbate interactions (Ofomaja et al., 2010) while the latter generally paints the picture of a more complex, multi-step process (Qiu et al., 2009). Seen from r values and the curves in Fig. 1, the adsorption of the two aldehydes was characterized by a speedy process, both concluded within 1 hr. Thus the pseudo first-order equation was the more suitable model.

The Elovich equation is one of the most useful models for describing chemisorption (Özacar and Şengil, 2005) and the constant b is related to the extent of surface coverage and activation energy for chemisorption. It was obvious that its predicted kinetic curves in Fig. 1 deviated from the experimental data, rendering it unacceptable. The Weber–Morris intraparticle diffusion model also did not fit well. This model assumes that the intraparticle diffusion step is the rate-limiting one. The intercept of the plot indicates the effect of external mass transfer: the larger the intercept, the greater the contribution of external mass transfer in the rate-limiting step (Vadivelan and Kumar, 2005). The intraparticle diffusion model fitting results all ended up with considerable intercepts and unsatisfactory r values. This proved that intraparticle diffusion was not the only factor governing the adsorption process.

The effect of PAC dosage on adsorption kinetics is shown in Fig. 2. It is clear that for both odorants, the variation of PAC dosage greatly altered the adsorption kinetics pattern: with higher dosage, the equilibrium was achieved in a shorter time span and a lower carbon loading was observed. The decrease in unit adsorption amount with the increase of PAC dosage was due to the fact that the adsorption sites remained unsaturated during the adsorption process (Shukla et al., 2002). The rate constants of the pseudo first-order kinetics model (k_1) and the pseudo second-order kinetics model (k_2) were studied (Fig. 3).
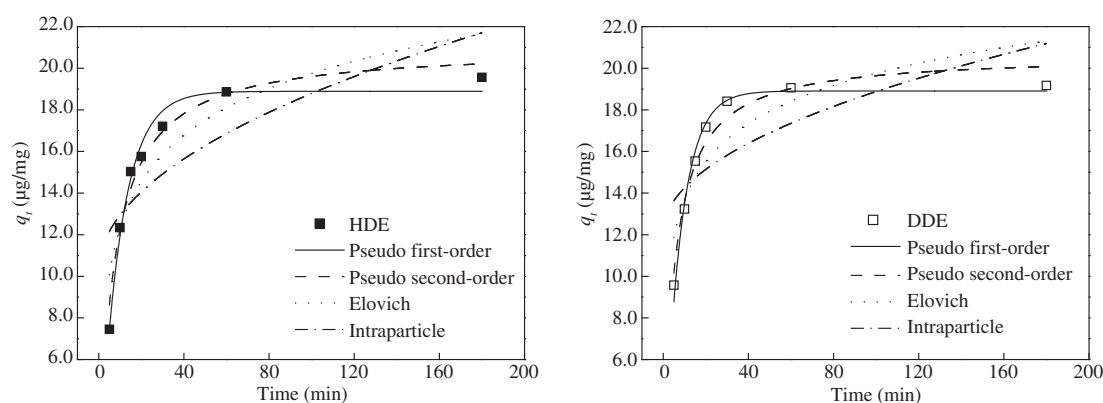
Fig. 1 – Adsorption kinetic curves of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) (powdered activated carbon dosage = 20 mg/L, c_0 = 400 μg/L, pH 7, temperature = 298 K).

As implied by Fig. 3, when PAC dosage increased from 5 to 25 mg/L, k_1 and k_2 values for both odorants increased. This can be attributed to greater surface area and availability of more adsorption sites with increasing adsorbent dosage (Demirbas et al., 2008, 2009; Ma et al., 2010; Geethakarthi and Phanikumar, 2011, 2012). Specifically, along with the increase of PAC dosage, k_1 rose from 0.0298 to 0.127 for HDE and from 0.0303 to 0.156 for DDE, while k_2 changed from 0.000370 to 0.0112 for HDE and from 0.000432 to 0.0.58 for DDE. It is clear that DDE had higher rate constants in both models under various PAC dosages, which is understandable from a molecular interaction perspective as discussed in Section 1.2.

2.2. Adsorption capacity

2.2.1. Curves of adsorption isotherms
The first approach to diagnose the nature of adsorption equilibria is to evaluate the shape of the isotherm curves. According to Giles et al. (1960), four classes of isotherms are often observed: S, L, H, and C curves. The tested plots of q_e vs. c_e are shown in Fig. 4. As depicted in the figure, experimental adsorption data for HDE and DDE took on an L curve pattern. The L curves are indicative of molecules adsorbed flat on the surface where there is no strong competition between solvent and adsorbate for adsorbent surface sites.

With the aim of precisely describing the experimental data with appropriate isotherm models and specifying model parameters, several isotherm models were employed. The experimental values of q_e and c_e were first treated with linearized forms of the models to obtain model parameters and correlation coefficients (r), then the isotherms were drawn using the determined parameters. In addition, the average percentage error (APE) of each model was calculated to reflect

the extent of fitting between the tested and predicted q_e. APE was obtained according to Eq. (3):

$$\text{APE} = \frac{\sum_{i=1}^{N} \left| (q_e)_{\text{experimental}} - (q_e)_{\text{predicted}} \right| / (q_e)_{\text{experimental}}}{N} \times 100\% \quad (3)$$

where, N is the number of experimental data.

2.2.2. Freundlich isotherm
The maximum adsorption capacity q_m (μg/mg) derived from the Freundlich equation can be determined by Eq. (4).

$$q_m = K_f c_0^{\frac{1}{n}} \quad (4)$$

The calculated parameters, correlation coefficients r, and APE for the Freundlich model are listed in Table 3. A good correlation was suggested by the values of r (>0.985) for both odorants. In addition, the APEs of Freundlich model fitting results were in an acceptable range, implying good predictability and precise description by the model. The adsorption capacity was represented by constant K_f, and DDE had a larger K_f value. A similar phenomenon was reflected by the difference of q_m values of the two odorants. The greater adsorption capacity of DDE might be attributed to its higher $\log K_{ow}$ value, which makes it easier to affiliate with the non-polar adsorbent. The exponent $1/n$ in the model is an indicator of adsorption favorability (Treybal, 1980). In general, a value of n in the range of 2–10 means good, 1–2 moderately difficult, and less than 1 poor. According to Table 3, values of n for HDE and DDE were between 2 and 10, implying high removal intensity by PAC (Hamdaoui and Naffrechoux, 2007).

2.2.3. Langmuir isotherm
The values of correlation coefficient (r > 0.985) in Table 3 suggested a strong agreement between the experimental data

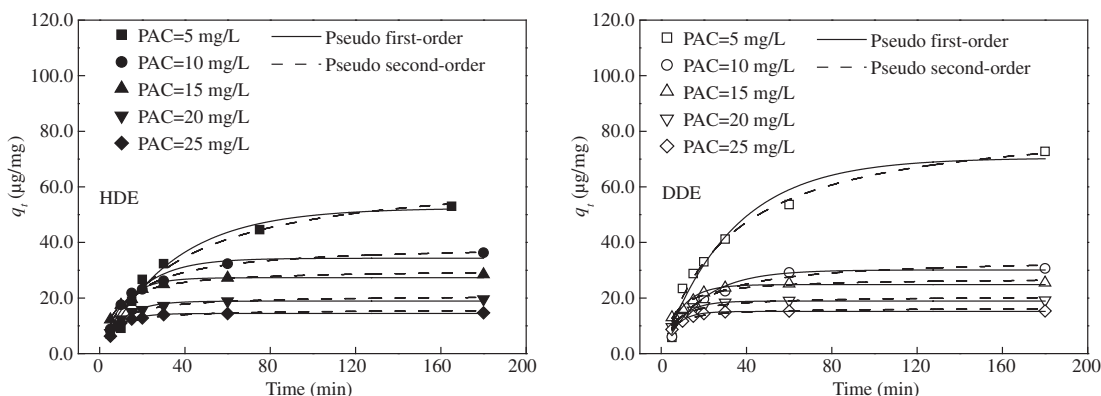| Table 2 – Kinetic parameters for powdered activated carbon adsorption of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE).								
Adsorbate	Pseudo first-order		Pseudo second-order		Elovich		Intraparticle diffusion	
	k_1	r	k_2	r	b	r	k_{int}	r
HDE	1.00×10^{-1}	0.991	6.62×10^{-3}	0.984	7.44	0.897	8.55×10^{-1}	0.726
DDE	1.25×10^{-1}	0.992	9.36×10^{-3}	0.981	6.07	0.854	6.76×10^{-1}	0.657

Fig. 2 – Adsorption kinetic curves of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) under different powdered activated carbon (PAC) dosage (c_0 = 400 μg/L, pH 7, temperature = 298 K).

and the Langmuir isotherm. However, the APE of the Langmuir model for either odorant was substantially larger than that of the Freundlich model, revealing that the Langmuir equation was not the best to describe the equilibrium data. Based on the hypothesis of heterogeneous adsorbent surfaces or heterogeneous adsorbent surface energies (Tan et al., 2008, 2009), the Freundlich isotherm assumes that the stronger binding sites are occupied first and that the binding strength decreases with increasing site occupation degree. The Langmuir model, conversely, assumes a monolayer adsorption onto a surface of uniform energies and no transmigration of adsorbate on the adsorbent surface (Hamdaoui and Naffrechoux, 2007; Tan et al., 2009). In the tested condition, the PAC surface energies were not uniform; hence the Langmuir model was not the best choice.

The Langmuir maximum carbon loading values for the two odorants were 135 μg/mg and 289 μg/mg, displaying the fact that the PAC uptake of DDE was higher than that of HDE. The favorability of adsorption could be assessed using Langmuir parameters in the equation of Hall et al. (1966) (Eq. (5)):
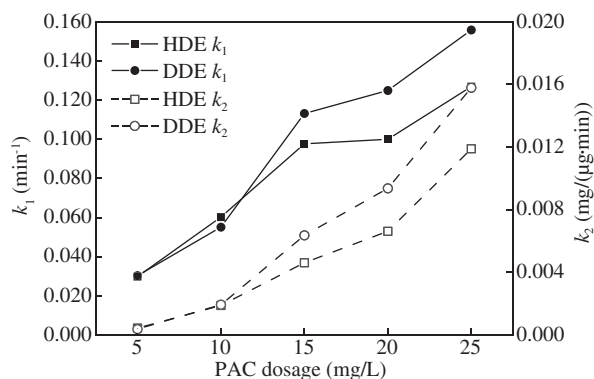
$$R_L = 1/(1 + bc_0) \tag{5}$$

Fig. 3 – Adsorption rate constants under different powdered activated carbon (PAC) dosage for trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) (c_0 = 400 μg/L, pH 7, temperature = 298 K).

where, R_L indicates the type of adsorption (R_L = 0, irreversible; $0 < R_L < 1$, favorable; R_L = 1, linear; $R_L > 1$, unfavorable).

The calculated R_L factors for HDE and DDE were 7.26×10^{-2} and 1.50×10^{-2}, meaning favorable adsorption occurred in each case.

2.2.4. Elovich isotherm
Seen in Table 3, the Elovich model exhibited fairly good coefficients of correlation (>0.95), but lower than those of the Freundlich equation and Langmuir model. In addition, the maximum adsorption capacities predicted by the Elovich model were much lower than the experimental data. The Elovich model assumes that the adsorption sites increase exponentially with adsorption, i.e., multilayer adsorption (Elovich and Larinov, 1962). The discrepancies of maximum adsorption capacities reflected the fact that the basic hypothesis of multilayer adsorption did not coincide with experimental results in the tested concentration range.

2.2.5. Modified Freundlich isotherm
Isotherm studies for NOM adsorption onto activated carbon demonstrated an adsorbent-dependence phenomenon (Karanfil and Kilduff, 1999; Hyung and Kim, 2008). This adsorbent-dosage normalized model has been found suitable in a wide range of studies (Summers and Roberts, 1988a,b; Kilduff et al., 1996, 1998). The coefficients of correlation of the Modified Freundlich model in Table 3 implied good linearity (>0.985) and the APE values were the smallest among all the studied models. Moreover, HDE gave a smaller K'_f value than did DDE, which is in line with the experimental data and the result of the Freundlich model.

2.2.6. Temkin isotherm
The employment of the Temkin equation requires the knowledge of the q_m value in advance so as to determine the fraction coverage (Table 1). It is reasonable to make use of the q_m values derived from Freundlich or Langmuir models. The parameters of the Temkin equation are listed in Table 4.

The Temkin isotherm assumes that the heat of adsorption decreases linearly along with surface coverage and that binding energies are uniformly distributed (Hamdaoui and Naffrechoux, 2007). As seen in Tables 3 and 4, values of the correlation coefficient were lower than the Langmuir ones but
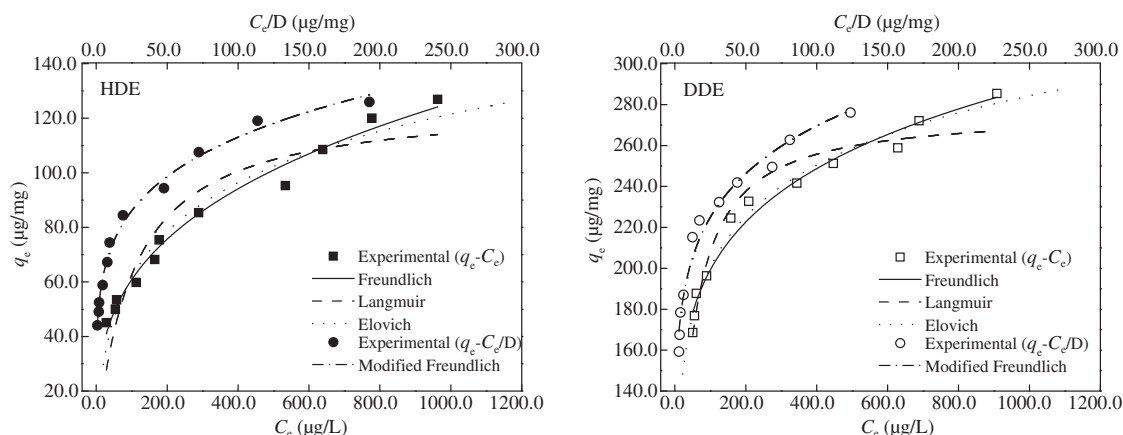
Fig. 4 – Adsorption isotherm of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) onto powdered activated carbon (pH 7, temperature = 298 K).

higher than the Elovich ones no matter what maximum carbon loading value was used. The adsorption energy variation, i.e., ΔQ, appeared to be positive for both odorants, implying an exothermic adsorption process. The values of average percentage error for the two off-flavor compounds were 7.35% and 2.11% and both were satisfactory for model fitting. Hence the Temkin equation could adequately describe the adsorption isotherms of HDE and DDE.

2.2.7. Summary of adsorption isotherms

According to the results and discussions above, the PAC adsorption isotherms of HDE and DDE could be well described by the Freundlich model in terms of correlation coefficient, APE, and the predicted maximum carbon loading. Other models showed deviations in data description or maximum carbon loading prediction. The surface of PAC was in general heterogeneous, and the binding energies were not uniformly distributed, which are in line with the hypothesis of the Freundlich model.

Besides, in the tested concentration range, multilayer adsorption was not achieved. Thus, the Freundlich model was able to accurately fit the experimental data.

2.3. Adsorption thermodynamics

The thermodynamic parameters for adsorption include the Gibbs free energy change ΔG^0 (kJ/mol), the enthalpy change ΔH^0 (kJ/mol), and the entropy change ΔS^0 (kJ/(mol·K)). These parameters can be determined as follows:

$$\Delta G^0 = -RT \ln K \tag{6}$$

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{7}$$

where, R (8.314 J/(mol·K)) is the universal gas constant, T (K) is the absolute temperature and K can be obtained from the Langmuir isotherm constant b (Wang et al., 2007b; Tan et al., 2009). Values of K at 298, 308, 318, and 328 K were used to determine the enthalpy change and the entropy change in Fig. 5. Values of ΔG^0 are listed in Table 5.

The negative values of ΔH^0 for both odorants indicated the exothermic nature of the adsorption. Generally, the enthalpy change for physical adsorption is usually in the range of nil to

Table 3 – Isotherm model parameters for the adsorption of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) onto powdered activated carbon.

Models	Parameters	HDE	DDE
Freundlich	K_f	15.4	93.5
	$1/n$	0.301	0.164
	q_m	142	346
	r	0.992	0.986
	Average percentage error (%)	3.89	2.27
Langmuir	b	8.00×10^{-3}	2.18×10^{-2}
	q_m	135	289
	r	0.988	0.998
	Average percentage error (%)	13.2	5.08
Elovich	K_E	9.92×10^{-2}	4.08
	q_m	36.0	44.2
	r	0.959	0.986
	Average percentage error (%)	6.21	2.08
Modified Freundlich	K'_f	46.1	154
	$1/n'$	0.197	0.130
	r	0.996	0.987
	Average percentage error (%)	2.63	2.17

Table 4 – Parameters of Temkin isotherm for powdered activated carbon adsorption of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE).

q_m		HDE	DDE
Derived from Freundlich isotherm	K_0	0.155	2.90
	ΔQ	15.0	24.3
	r	0.972	0.989
	Average percentage error (%)	7.35	2.11
Derived from Langmuir isotherm	K_0	0.155	2.90
	ΔQ	14.2	20.2
	r	0.972	0.989
	Average percentage error (%)	7.35	2.11

–42 kJ/mol, and that for chemical adsorption is in the range of –42 to –125 kJ/mol (Wang et al., 2007b). Thus it is obvious from the table that the PAC adsorption of the two compounds could be considered as physical adsorption. Meanwhile, the negative ΔG^0 values indicated that the adsorption process was feasible and spontaneous (Bilgili, 2006). The change of Gibbs free energy for physical adsorption is generally in the range of nil to –20 kJ/mol, and that for chemical adsorption is in the range of –80 to –400 kJ/mol (Wang et al., 2006). The values of ΔG^0 at different temperatures for the two odorants again proved that the adsorption of HDE and DDE onto PAC was mainly a physical adsorption process.

2.4. Effect of initial pH

Isotherms of HDE and DDE under different pH conditions are depicted in Fig. 6. It could be concluded that in the tested concentration range, both odorants had progressively higher adsorption capacities when pH increased from 3 to 7, and adsorption capacities at pH 11 were generally lower than those at pH 7 or pH 9. In order to fully investigate the effect of pH on adsorption capacity, q_m values derived from the Freundlich and Langmuir models were introduced in the study, and the influence of pH on q_m is shown in Fig. 7.

As seen in Fig. 7, the Freundlich maximum adsorption capacity of HDE rose from 125 to 196 μg/mg when pH increased from 3 to 9, and then decreased to 131 μg/mg at pH 11. Similarly, the Langmuir maximum adsorption capacity of HDE rose from 105 to 173 μg/mg when pH increased from 3 to 9, and then dropped to 102 μg/mg at pH 11. As for DDE, the Freundlich q_m increased from 311 to 370 μg/mg with pH increasing from 3 to 9, and then dropped to 342 μg/mg at pH 11. Meanwhile, the Langmuir q_m saw a rise from 285 to 314 μg/mg from pH 3 to 9 and went down to 305 μg/mg at pH 11.

Both odorants exhibited higher q_m values at pH 9, which could be explained from the viewpoint of intermolecular forces. Two interactions, *i.e.*, non-electrostatic interactions (including dispersion and hydrophobic interactions) and electrostatic interactions, composed the main forces in the adsorption process
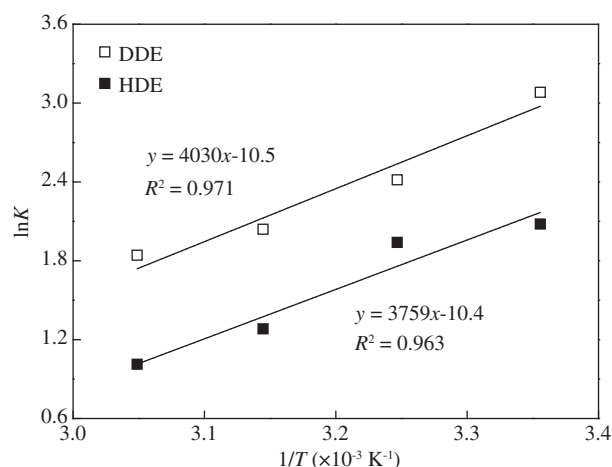

Fig. 5 – lnK vs. 1/T plot for the determination of thermodynamic parameters of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal.

Table 5 – Thermodynamic parameters for trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) adsorption on powdered activated carbon.				
	T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/(mol·K))
HDE	298	–5.38	–31.2	-8.68×10^{-3}
	308	–4.52		
	318	–3.65		
	328	–2.78		
DDE	298	–7.36	–33.5	-8.77×10^{-3}
	308	–6.49		
	318	–5.61		
	328	–4.73		

(Moreno-Castilla, 2004). In addition, the solution pH has influence on not only the ionization of compounds of interest but also the surface charge of the adsorbent (El Qada et al., 2006). For HDE and DDE, pH had no influence on their molecular charge since they possess no ionizable groups. Thus the variation of maximum adsorption capacity under different pH conditions was due to the change of PAC surface charge. The pH_{pzc} of an adsorbent is where the adsorbent has a net charge of zero on its surface (Sparks, 2002). In general, if the pH of solution is below the adsorbent's pH_{pzc}, the surface has a net positive charge because of excessive H^+ ions. On the contrary, if the pH is higher than pH_{pzc}, the net charge is negative (Kubilay et al., 2007). The plot to determine the point of zero charge of PAC is shown in Fig. 8.

The point of zero charge of the PAC used was observed at pH 9.45, which implied that at pH 9, the PAC surface had minimum net charge compared with that under other tested conditions. Therefore, at pH lower than 9, positive charges on the surface of adsorbent would adversely influence adsorption, leading to smaller adsorption capacity. At the same time, when solution pH was 11, the PAC surface gained negative charges, undermining the interaction between odorants and adsorbent. Thus, pH 9 exhibited the most favorable condition for adsorption of all tested pH values.

According to the results and discussion presented in previous sections, a mechanism analysis for HDE and DDE adsorption onto PAC could be conducted. As mentioned above, non-electrostatic interactions and electrostatic interactions are the two main forces for adsorption. In the study of pH effect, the electrostatic attraction was ruled out as the governing factor. Research has shown that for the adsorption of phenols and chlorophenols, the π–π interaction is the controlling mechanism (Jung et al., 2001; Wang et al., 2007a). The π–π interaction could also occur between the PAC surface and organic molecules with carbon–carbon double bonds (Pan and Xing, 2008). However, this mechanism could not explain the adsorption capacity difference between the two odorants. Thus, as discussed in the isotherm studies, the governing factor for HDE and DDE adsorption was the hydrophobic interactions, reflected by the differences of their logK_{ow} values and solubility (2.80 g/L for HDE and 0.106 g/L for DDE, generated using the US Environmental Protection Agency's EPISuite™).

2.5. Effect of NOM

In order to investigate the effect of NOM on adsorption, two groups of experiments were conducted. In the first one, 3 mg/L
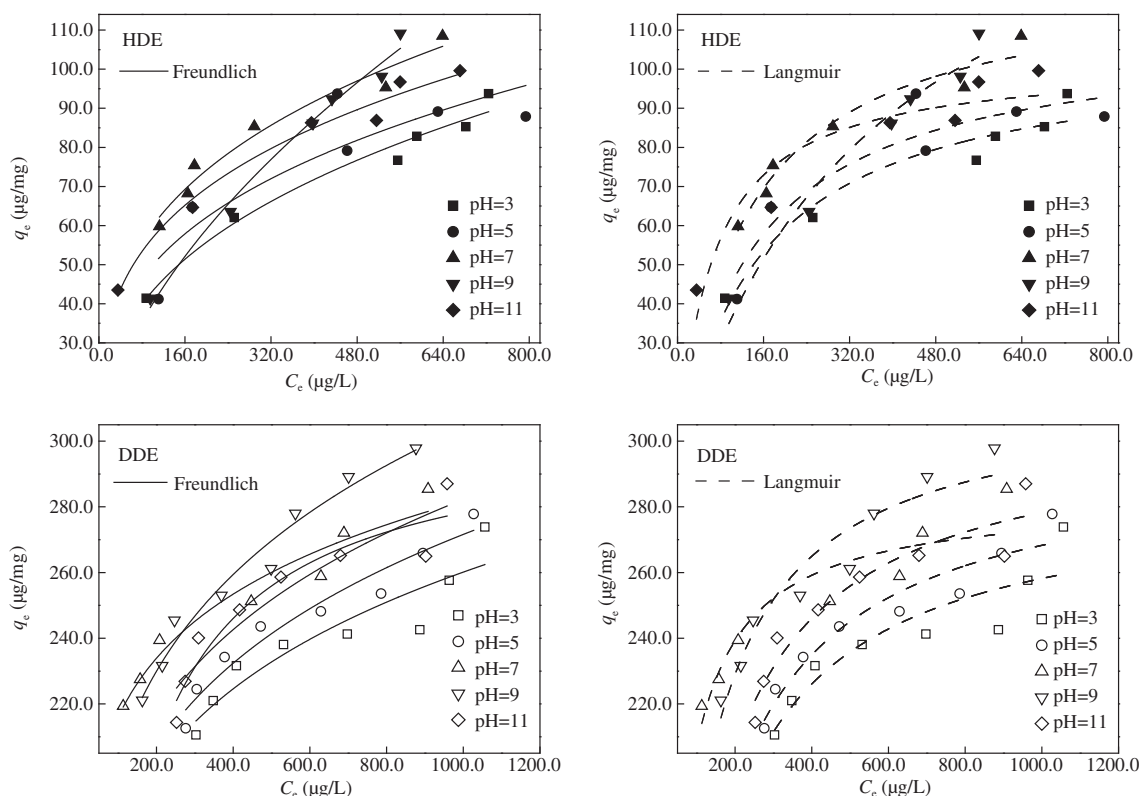
Fig. 6 – Adsorption isotherms of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) under different pH (temperature = 298 K).

NOM was simultaneously added with a certain amount of odorant into bottles containing 5 mg/L PAC for adsorption. For the other group, PAC was allowed to reach equilibrium adsorption of NOM for 48 hr and then the odorant was fed and adsorbed by the preloaded PAC. The results are depicted in Fig. 9.

For HDE, 5 mg/L PAC was able to remove 20.5% of the odorant with initial concentration of 2.5 mg/L without background NOM. On the other hand, 84.6% of the original 1 mg/L DDE was adsorbed by 5 mg/L PAC without background NOM. It is clear in the figure that the presence of NOM inhibited the adsorption of the two odorants to different extent. For both odorous compounds, the inhibition effect grew larger with the decrease of NOM molecular weight. Specifically, the bulk NOM displayed a slight adverse effect on adsorption, while the
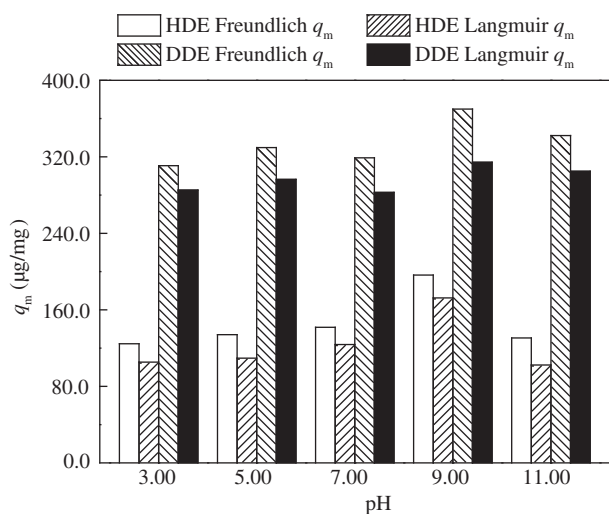
Fig. 7 – Effect of pH on q_m for powdered activated carbon adsorbing trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE).
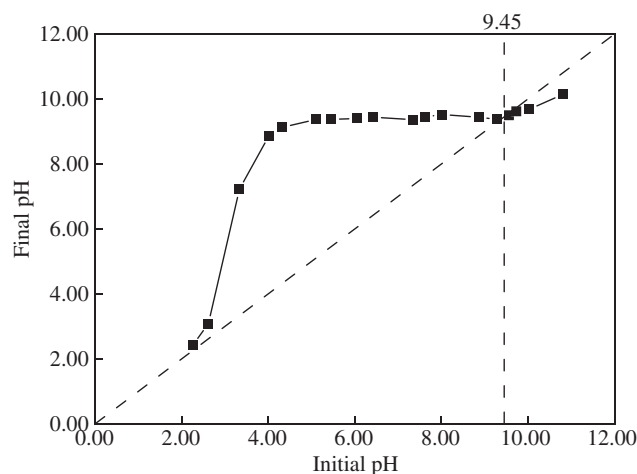
Fig. 8 – Determination of point of zero charge for powdered activated carbon.
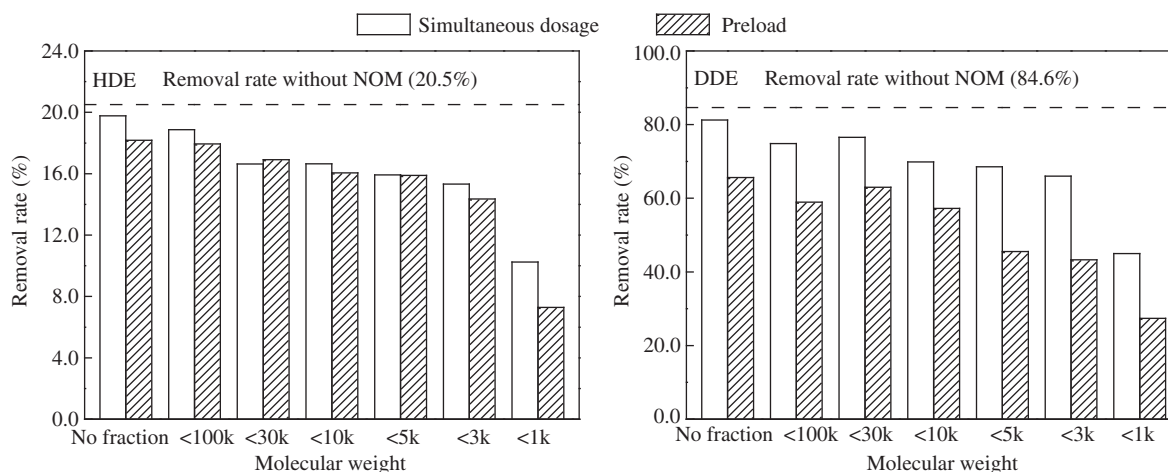
Fig. 9 – Removal rate of trans,trans-2,4-heptadienal (HDE) and trans,trans-2,4-decadienal (DDE) with background natural organic matters.

NOM fraction with MW less than 1 k Da reduced the removal rate of HDE and DDE to less than 10% and 50% respectively.

The main mechanism involved in the adsorption of the two aldehydes is hydrophobic attraction, thus the adsorption capacity relies on the volume of appropriate size pores, i.e., micropores, available (Newcombe et al., 1997); and the available amount of pores is mostly influenced by the NOM fraction with MW <1000. The larger size fractions are not in direct competition with the compounds of interest since they predominantly take up the larger pores. Therefore, with constant initial NOM of 3 mg/L, the more intense competition occurred as the nominal molecular weight decreased.

Furthermore, the removal efficiency of adsorption was reduced more by the preloaded NOM than by the simultaneously dosed NOM. Seen in the figure, the preloaded PAC had 2%–4% lower removal rate for HDE than in the simultaneous dosage situation for every NOM molecular weight fraction. The trend was more evident for DDE, where a 10%–20% reduction of adsorption rate was observed.

In addition to direct competition with the target compound, the preloaded NOM could adversely affect adsorption in ways such as (1) blocking access to micropores, (2) keeping odorants away from the nonpolar regions on the PAC surface, and (3) reducing the interaction energy between adsorbent and adsorbate (Müller et al., 2000; Matsui et al., 2002). Moreover, Kilduff et al. (1998) reported that the preloaded NOM would reduce the number of high-energy adsorption sites, leading to substantial loss of adsorption capacity. Hence the preloading of NOM could greatly affect the adsorption of HDE and DDE onto PAC, which should be considered in practical application.

3. Conclusions

This study provided a deep insight into PAC adsorption of HDE and DDE through the investigation of adsorption kinetics, isotherms, thermodynamics, and influencing factors. For kinetics, the pseudo first-order and pseudo second-order kinetic models could well describe the kinetic patterns, with DDE having higher kinetic rate constants. In isotherm tests, Freundlich and

Modified Freundlich isotherms sufficiently predicted the adsorption capacity. The higher hydrophobicity of DDE led to a higher adsorption capacity on PAC. The thermodynamic study revealed the exothermic nature of the adsorption and proved that the process was spontaneous and feasible. PAC dosage had a positive influence on the rate constants of both the pseudo first-order model and the pseudo second-order model. At pH 9, a pH value near the pH_{pzc} of PAC, maximum adsorption of the two odorants was observed. The preloaded NOM inhibited the adsorption of HDE and DDE more significantly than the simultaneously added NOM.

REFERENCES

Bilgili, M.S., 2006. Adsorption of 4-chlorophenol from aqueous solutions by XAD-4 resin: isotherm, kinetic, and thermodynamic analysis. J. Hazard. Mater. 137 (1), 157–164.

Demirbas, E., Kobya, M., Sulak, M.T., 2008. Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon. Bioresour. Technol. 99 (13), 5368–5373.

Demirbas, E., Dizge, N., Sulak, M.T., Kobya, M., 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. Chem. Eng. J. 148 (2–3), 480–487.

El Qada, E.N., Allen, S.J., Walker, G.M., 2006. Adsorption of methylene blue onto activated carbon produced from steam activated bituminous coal: a study of equilibrium adsorption isotherm. Chem. Eng. J. 124 (1–3), 103–110.

Elovich, S.Y., Larinov, O.G., 1962. Theory of adsorption from solutions of non electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form, (II) verification of the equation of adsorption isotherm from solutions. Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk. 2 (2), 209–216.

Geethakarthi, A., Phanikumar, B.R., 2011. Adsorption of reactive dyes from aqueous solutions by tannery sludge developed activated carbon: kinetic and equilibrium studies. Int. J. Environ. Sci. Technol. 8 (3), 561–570.

Geethakarthi, A., Phanikumar, B.R., 2012. Characterization of tannery sludge activated carbon and its utilization in the removal of azo reactive dye. Environ. Sci. Pollut. Res. 19 (3), 656–665.

Gerber, N.N., Lechevalier, H.A., 1965. Geosmin, an earthy-smelling substance isolated from actinomycetes. Appl. Microbiol. 13 (6), 935–938.

Giles, C.H., MacEwan, T.H., Nakhwa, S.N., Smith, D., 1960. 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc. 3973–3993 (Resumed).

Hall, K.R., Eagleton, L.C., Acrivos, A., Vermeulen, T., 1966. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind. Eng. Chem. Fundam. 5 (2), 212–223.

Hamdaoui, O., Naffrechoux, E., 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. J. Hazard. Mater. 147 (1–2), 381–394.

Hockelmann, C., Jüttner, F., 2005. Off-flavours in water: hydroxyketones and beta-ionone derivatives as new odour compounds of freshwater cyanobacteria. Flavour Frag. J. 20 (4), 387–394.

Hyung, H., Kim, J., 2008. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters. Environ. Sci. Technol. 42 (12), 4416–4421.

Jo, C.H., 2008. Oxidation of Disinfection Byproducts and Algae-related Odorants by UV/H_2O_2. (PhD thesis). Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA.

Jung, M., Ahn, K., Lee, Y., Kim, K., Rhee, J., Tae Park, J., et al., 2001. Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC). Microchem. J. 70 (2), 123–131.

Jüttner, F., 1995. Physiology and biochemistry of odorous compounds from freshwater cyanobacteria and algae. Water Sci. Technol. 31 (11), 69–78.

Jüttner, F., 2001. Liberation of 5,8,11,14,17-eicosapentaenoic acid and other polyunsaturated fatty acids from lipids as a grazer defense reaction in epilithic diatom biofilms. J. Phycol. 37 (5), 744–755.

Karanfil, T., Kilduff, J.E., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 1. Priority pollutants. Environ. Sci. Technol. 33 (18), 3217–3224.

Khiari, D., Suffet, I.H., Barrett, S.E., 1995. The determination of compounds causing fishy/swampy odors in drinking-water supplies. Water Sci. Technol. 31 (11), 105–112.

Kilduff, J.E., Karanfil, T., Chin, Y., Weber, W.J., 1996. Adsorption of natural organic polyelectrolytes by activated carbon: a size-exclusion chromatography study. Environ. Sci. Technol. 30 (4), 1336–1343.

Kilduff, J.E., Karanfil, T., Weber Jr., W.J., 1998. Competitive effects of nondisplaceable organic compounds on trichloroethylene uptake by activated carbon. II. Model verification and applicability to natural organic matter. J. Colloid Interface Sci. 205 (2), 280–289.

Kim, Y., Lee, Y., Gee, C.S., Choi, E., 1997. Treatment of taste and odor causing substances in drinking water. Water Sci. Technol. 35 (8), 29–36.

Kubilay, Ş., Gürkan, R., Savran, A., Şahan, T., 2007. Removal of Cu (II), Zn (II) and Co (II) ions from aqueous solutions by adsorption onto natural bentonite. Adsorption 13 (1), 41–51.

Lazaridis, N.K., Asouhidou, D.D., 2003. Kinetics of sorptive removal of chromium (VI) from aqueous solutions by calcined Mg-Al-CO_3 hydrotalcite. Water Res. 37 (12), 2875–2882.

Ma, J.W., Wang, H., Wang, F.Y., Huang, Z.H., 2010. Adsorption of 2,4-dichlorophenol from aqueous solution by a new low-cost adsorbent-activated bamboo charcoal. Sep. Sci. Technol. 45 (16), 2329–2336.

Matsui, Y., Knappe, D.R., Takagi, R., 2002. Pesticide adsorption by granular activated carbon adsorbers. 1. Effect of natural organic matter preloading on removal rates and model simplification. Environ. Sci. Technol. 36 (15), 3426–3431.

Miralto, A., Barone, G., Romano, G., Poulet, S.A., Ianora, A., Russo, G.L., et al., 1999. The insidious effect of diatoms on copepod reproduction. Nature 402 (6758), 173–176.

Moreno-Castilla, C., 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon 42 (1), 83–94.

Müller, E.A., Hung, F.R., Gubbins, K.E., 2000. Adsorption of water vapor-methane mixtures on activated carbons. Langmuir 16 (12), 5418–5424.

Newcombe, G., Drikas, M., Hayes, R., 1997. Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. Water Res. 31 (5), 1065–1073.

Ofomaja, A.E., Naidoo, E.B., Modise, S.J., 2010. Kinetic and pseudo-second-order modeling of lead biosorption onto pine cone powder. Ind. Eng. Chem. Res. 49 (6), 2562–2572.

Órfão, J.J.M., Silva, A.I.M., Pereira, J.C.V., Barata, S.A., Fonseca, I.M., Faria, P.C.C., et al., 2006. Adsorption of a reactive dye on chemically modified activated carbons—influence of pH. J. Colloid Interface Sci. 296 (2), 480–489.

Özacar, M., Şengil, İ.A., 2005. A kinetic study of metal complex dye sorption onto pine sawdust. Process Biochem. 40 (2), 565–572.

Pan, B., Xing, B.S., 2008. Adsorption mechanisms of organic chemicals on carbon nanotubes. Environ. Sci. Technol. 42 (24), 9005–9013.

Peter, A., Köster, O., Schildknecht, A., Von Gunten, U., 2009. Occurrence of dissolved and particle-bound taste and odor compounds in Swiss lake waters. Water Res. 43 (8), 2191–2200.

Qiu, H., Lü, L., Pan, B.C., Zhang, Q.J., Zhang, W.M., Zhang, Q.X., 2009. Critical review in adsorption kinetic models. J. Zhejiang Univ. Sci. A 10 (5), 716–724.

Satchwill, T., Watson, S.B., Dixon, E., 2007. Odourous algal-derived alkenes: differences in stability and treatment responses in drinking water. Water Sci. Technol. 55 (5), 95–102.

Shukla, A., Zhang, Y.H., Dubey, P., Margrave, J.L., Shukla, S.S., 2002. The role of sawdust in the removal of unwanted materials from water. J. Hazard. Mater. 95 (1–2), 137–152.

Sparks, D.L., 2002. Environmental Soil Chemistry. 2nd ed. Academic Press, Massachusetts, USA.

Suffet, I.H., Khiari, D., Mallevialle, J., 1996. Taste and odor problems in drinking water. In: Saxby, M.J. (Ed.), Food Taints and Off-flavours. Springer, New York, pp. 107–138.

Suffet, I.H., Khiari, D., Bruchet, A., 1999. The drinking water taste and odor wheel for the millennium: beyond geosmin and 2-methylisoborneol. Water Sci. Technol. 40 (6), 1–13.

Summers, R.S., Roberts, P.V., 1988a. Activated carbon adsorption of humic substances: I. Heterodisperse mixtures and desorption. J. Colloid Interface Sci. 122 (2), 367–381.

Summers, R.S., Roberts, P.V., 1988b. Activated carbon adsorption of humic substances: II. Size exclusion and electrostatic interactions. J. Colloid Interface Sci. 122 (2), 382–397.

Tan, I.A.W., Ahmad, A.L., Hameed, B.H., 2008. Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. Desalination 225 (1–3), 13–28.

Tan, I.A.W., Ahmad, A.L., Hameed, B.H., 2009. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. J. Hazard. Mater. 164 (2–3), 473–482.

Treybal, R.E., 1980. Mass-transfer Operations. 3rd ed. McGraw-Hill, New York, USA.

Vadivelan, V., Kumar, K.V., 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J. Colloid Interface Sci. 286 (1), 90–100.

Wang, Y., Mu, Y., Zhao, Q.B., Yu, H.Q., 2006. Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge. Sep. Purif. Technol. 50 (1), 1–7.

Wang, J.P., Chen, Y.Z., Feng, H.M., Zhang, S.J., Yu, H.Q., 2007a. Removal of 2,4-dichlorophenol from aqueous solution by static-air-activated carbon fibers. J. Colloid Interface Sci. 313 (1), 80–85.

Wang, J.P., Feng, H.M., Yu, H.Q., 2007b. Analysis of adsorption characteristics of 2,4-dichlorophenol from aqueous solutions by activated carbon fiber. J. Hazard. Mater. 144 (1–2), 200–207.

Watson, S.B., 2004. Aquatic taste and odor: a primary signal of drinking-water integrity. J. Toxicol. Environ. Health A 67 (20–22), 1779–1795.

Watson, S.B., Satchwill, T., 2003. Chrysophyte odour production: resource-mediated changes at the cell and population levels. Phycologia 42 (4), 393–405.

Watson, S.B., Satchwill, T., Dixon, E., McCauley, E., 2001. Under-ice blooms and source-water odour in a nutrient-poor reservoir: biological, ecological and applied perspectives. Freshw. Biol. 46 (11), 1553–1567.

Wnorowski, A.U., 1992. Tastes and odours in the aquatic environment: a review. Water SA 18 (3), 203–214.

Yang, M., Yu, J., Li, Z., Guo, Z., Burch, M., Lin, T.F., 2008. Taihu Lake not to blame for Wuxi's woes. Science 319 (5860), 158.

Yano, H., Nakahara, M., Ito, H., 1988. Water blooms of *Uroglena americana* and the identification of odorous compounds. Water Sci. Technol. 20 (8–9), 75–80.

Young, C.C., Suffet, I.H., Crozes, G., Bruchet, A., 1999. Identification of a woody-hay odor-causing compound in a drinking water supply. Water Sci. Technol. 40 (6), 273–278.

Zhang, X.J., Chen, C., Ding, J.Q., Hou, A., Li, Y., Niu, Z.B., et al., 2010. The 2007 water crisis in Wuxi, China: analysis of the origin. J. Hazard. Mater. 182 (1–3), 130–135.

Zhang, X.J., Chen, C., Lin, P.F., Hou, A.X., Niu, Z.B., Wang, J., 2011. Emergency drinking water treatment during source water pollution accidents in China: origin analysis, framework and technologies. Environ. Sci. Technol. 45 (1), 161–167.

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