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Sorption and degradation of bisphenol A by aerobic activated sludge

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Abstract

Laboratory-scale batch experiments were conducted to investigate the sorption and degradation of bisphenol A (BPA) at μ g/L range in an aerobic activated sludge system. The sorption isotherms and thermodynamics indicated that the sorption of BPA on sludge was mainly a physical process in which partitioning played a dominating role. The values of sorption coefficient K_{oc} were between 621 and 736 L/kg in the temperature range of 10–30 °C. Both mixed liquor suspended solid (MLSS) and temperature influenced BPA sorption on sludge. The degradation of BPA by acclimated activated sludge could be described by first-order reaction equation with the first-order degradation rate constant of 0.80 h⁻¹ at 20 °C. The decrease of initial COD concentration and the increase of MLSS concentration and temperature enhanced BPA degradation rate. The removal of BPA in the activated sludge system was characterized by a quick sorption on the activated sludge and subsequent biodegradation. © 2007 Elsevier B.V. All rights reserved.

Keywords: Bisphenol A; Sorption; Degradation; Aerobic; Activated sludge

1. Introduction

Bisphenol A (BPA) is an intermediate in the production of polycarbonate plastics and epoxy resins [1,2]. Because of wide usage of polycarbonate plastics and epoxy resins in industry and households, BPA has become one of the most ubiquitous contaminants in the environment [3,4]. BPA is slightly to moderately toxic to fish and invertebrates [1], and it is found to be a weakly estrogenic chemical [2,5]. Therefore, increasing interests have been generated over its fate in the environment and its elimination in waste treatment systems.

Effluent of wastewater treatment plants (WWTPs) is a major source for BPA entering rivers, streams and other surface waters. BPA has been detected in both influent and effluent as well as the sludge in WWTPs [6–8]. Fürhacker et al. [6] investigated BPA sources of a municipal WWTP in Lower Austria, and identified a paper mill facility as the major BPA contributor. They also determined BPA concentrations in the effluent of the facility ranged from 28 to 72 μ g/L. In their study, BPA was also detected in household sewage and the maximum concentration was as high as 5.8 μ g/L. Lee and Peart [8] conducted a largescale study on BPA contamination in Canadian sewage treatment

0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.11.075 plants (STPs), and found BPA contamination in all of the 72 sewage samples. The concentrations of BPA ranged from 0.08 to 4.98 μ g/L for the influent, and from 0.01 to 1.08 μ g/L for the effluent. They also discovered that BPA accumulation in sewage sludge was between 0.033 and 36.7 μ g/g (on a dry weight basis).

Although WWTPs with activated sludge process can eliminate BPA, the removal efficiency of BPA may vary markedly for different WWTPs [7-9]. Körner et al. [7] determined the concentration of estrogenic active compounds in a modern STP with biological nitrogen and phosphorus removal by activated sludge system in Germany, and concluded that 70% and 91% of BPA was removed in March and June, respectively. By examining the fate of BPA in 31 municipal STPs in Canada, Lee and Peart [8] found the removal efficiencies fell in the range of 37-94%. BPA was one of the 6 estrogenic disrupting chemicals that were detected in both influents and effluents of 27 WWTPs in Japan [9]. The mean BPA removal efficiency in these plants was more than 90%. The considerable removal differences of BPA in full-scale STPs may result from the differences in the type of plants, operational conditions, and the composition of influents. For two plants with the same treatment process and influent characteristics, the removal efficiencies might differ due to different operational conditions. Because operational conditions are easy to be controlled, it is feasible to investigate the effects of operational parameters using batch experiments so that enhancement in BPA removal by activated sludge process may

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be identified. For this purpose, batch degradation studies were conducted with non-acclimated sludge and some influential factors were studied [10]. As BPA pollution commonly exists in municipal wastewater and acclimation of sludge can influence the degradation behavior of chemicals even at trace concentration [11], it is necessary to study BPA degradation by acclimated sludge.

In WWTPs, contaminants are usually removed by processes such as biodegradation, sorption, volatilization, etc. The low vapor pressure of BPA $(8.7 \times 10^{-10} \text{ to } 3.96 \times 10^{-7} \text{ mm Hg})$ [1] indicates its poor volatilization during the treatment process. A relatively high octanol–water partition coefficient (log $K_{ow} = 2.2-3.82$) of BPA [1] suggests that sorption may be effective mechanism in addition to biodegradation. So far, studies on BPA sorption mainly focused on its sorption on sediments and soils [12–14], and the sorption of BPA on sludge is likely to be different because of the different chemical composition and properties of sludge.

In this study, laboratory-scale batch experiments were conducted to investigate the sorption and degradation of BPA at μ g/L range by aerobic activated sludge. For degradation tests, acclimated sludge by BPA was used. Because trace amount of BPA coexisted with other pollutants in WWTPs, the influence of COD is needed. Furthermore, the effects of temperature and mixed liquor suspended solid (MLSS) concentration on BPA sorption and degradation were also investigated to provide quantitative information of the behavior of BPA in activated sludge system.

2. Materials and methods

2.1. Chemicals

Bisphenol A was obtained from Aldrich (Milwaukee, WI, USA). HPLC grade acetonitrile and methanol were purchased from Merck (Darmstadt, Germany). The standard stock solution of BPA (10,000 mg/L) was prepared in methanol, and was diluted to standard work solution (10 mg/L) using deionized water before it was used for sorption and degradation experiments. Other chemicals used in this study were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Seed activated sludge and synthetic wastewater

Inoculated activated sludge was obtained from Shanghai Changqiao Municipal Wastewater Treatment Plant, China. The sludge was incubated in an 8 L reactor in the laboratory, fed with synthetic wastewater without BPA. The synthetic wastewater was composed of tap water, supplemented with nutrients, trace elements, and buffering compounds (Table 1). The average COD of the synthesized wastewater was 380 mg/L. The reactor was operated in a SBR mode with two cycles every day. Each cycle included 15 min filling, followed by 10 h aeration, 1.5 h settling, and 15 min drawing. The sludge retention time (SRT) was 25 days. After 2 months, COD of the effluent and MLSS in the reactor were stabilized in the range of 32–45 and 3000–3200 mg/L, respectively. This sludge was used for

Table 1Composition of the synthetic wastewater

Compound	Concentration (mg/L)		
C ₆ H ₁₂ O ₆	150		
Peptone	150		
NaAc	80		
NH ₄ Cl	76.4		
KH ₂ PO ₄ ·2H ₂ O	26.3		
MgSO ₄ ·7H ₂ O	20		
CaCl ₂	10.6		
NaHCO ₃	125		
FeCl ₃ ·6H ₂ O	0.45		
H ₃ BO ₃	0.045		
CuSO ₄ ·5H ₂ O	0.009		
KI	0.054		
MnCl ₂ ·4H ₂ O	0.036		
ZnSO ₄ ·7H ₂ O	0.036		
EDTA	3		

the sorption experiments. After the sorption experiments were complete, the activated sludge in the reactor was acclimated by spiking 10 μ g/L of BPA to the synthesized wastewater. After 2-month incubation, BPA removal efficiency was steadily above 90% and MLSS was in the range of 3000–3300 mg/L. The activated sludge was then used for BPA degradation experiments. The fraction of organic carbon (f_{oc}) of the sludge was measured by Shimadzu TOC-VCPN analyzer (Japan) with SSM-5000A solid burning device.

2.3. Sorption experiments

The sorption experiments were performed with sterilized sludge to avoid the influence of BPA degradation. The sterilization procedure was modified according to the method used by Wang and Grady [15]. They found that sorption isotherms of di-n-butyl phthalate on the live and sterilized biomass were the same when the loss of biomass during autoclaving was considered. Therefore, it is reasonable to use the sterilized sludge presenting the sorption performance of activated sludge. The sludge sample was taken from the incubation reactor and subsequently sterilized using an autoclave at 120 °C for 30 min. The sludge was then centrifuged and washed using tap water for three times. After the last centrifugation, the sludge was dissolved in the solution containing mineral media described in Table 1 to the MLSS level of 6000 mg/L, and stored in a refrigerator at 4 °C. Immediately before the sorption experiments, the sludge was diluted to the required MLSS level with the same mineral solution, and the initial pH of the mixed liquor was adjusted to 7.0. All the sorption experiments were carried out in duplicate.

The sorption experiments were conducted using 150-mL Erlenmeyer flasks. To determine the sorption equilibrium time, the flasks were filled with 100 mL sterilized sludge solution, and spiked with BPA standard work solution. The initial BPA concentration and MLSS was 100 μ g/L and 2000 mg/L, respectively. The flasks were immediately sealed with rubber plugs and were shaken on a thermostatic rotary shaker at 125 rpm and 20 °C. Samples were collected from the flasks at 0.25, 0.5, 1, 2, 5, 10, 14, and 24 h. The mixed liquor was centrifuged at 6000 rpm

for 10 min and the supernatant was filtrated through a glass fiber filter (GF/F, 0.45 μ m). The filtrate samples were acidified to pH 2 by 1 M HCl and stored in a refrigerator at 4 °C before they were extracted by SPE and analyzed by HPLC. Controls of the same initial BPA concentration without sludge were also prepared at the same laboratory condition and no significant loss was found.

After the sorption equilibrium time was determined, it is necessary to determine the sorption isotherms and investigate the effects of temperature on the sorption. The sorption isotherms were developed using MLSS of 2000 mg/L and BPA concentrations of 2, 10, 20, 50, and 100 μ g/L. The MLSS effect was examined using 20 μ g/L BPA concentration and MLSS concentrations of 1000, 2000, 3000, and 4000 mg/L. The temperature effect was studied under the condition of BPA concentrations of 2, 10, 20, 50, and 100 μ g/L and temperatures of 10, 20, and 30 °C, respectively. Other experimental conditions and sample preparation procedures were the same as those in the sorption equilibrium tests. Sorption of chemicals from a solution to a solid phase can be described by empirical Freundlich equation:

$$q = K_{\rm f} C_{\rm e}^{1/n} \tag{1}$$

where *q* is the quantity of a chemical sorbed to the solid phase (μ g/kg); *C*_e is equilibrated concentration of the chemical in solution (μ g/L). *K*_f is Freundlich sorption coefficient (μ g^(1-1/n)L^{1/n}/kg); 1/*n* is Freundlich exponent related to sorption mechanism.

When the value of n is unity, Freundlich model turns into simple linear sorption model which describe the sorption as the partitioning between the liquid and solid phases:

$$q = K_{\rm d}C_{\rm e} \tag{2}$$

where K_d is the linear sorption coefficient (L/kg), which is also called as the distribution coefficient of the target chemical between the liquid and solid phases. In addition, K_{oc} (L/kg) which relates K_d value to organic carbon content (f_{oc}) of the sorbent is also used to describe the sorption capacity of a sorbent. K_{oc} can be calculated according to the following equation:

$$K_{\rm oc} = \frac{K_{\rm d}}{f_{\rm oc}} \tag{3}$$

The sorption thermodynamics can be described by the Gibbs equations [16]:

$$\Delta G^{\circ} = -RT \ln K \tag{4}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \,\Delta S^{\circ} \tag{5}$$

From Eqs. (4) and (5), the following equation can be obtained:

$$\ln K = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \tag{6}$$

where ΔS° (J/(mol K)) and ΔH° (kJ/mol) are standard entropy and enthalpy for the sorption process, ΔG° the Gibbs free energy (kJ/mol), *R* the ideal gas constant (J/(mol K)). *T* the temperature (K), and *K* is the equilibrium sorption coefficient that can be expressed by K_d .

2.4. Degradation experiments

The BPA degradation experiments were conducted using 500-mL Erlenmeyer flasks. Acclimated activated sludge was taken from the incubation reactor and washed with tap water three times to remove the residual BPA. The sludge was then aerated for 12 h to allow the residual BPA in the sludge to be completely degraded. Preliminary results for determining the residual BPA in water and sludge phases after 12-h aeration indicated that BPA in both phases were below the detection limits (<15 ng/L in water phase and <120 µg/kg in sludge). After gravity separation, the supernatant was decanted, and the sludge was evenly distributed into several flasks. Mixed liquor of 200 mL with 20 µg/L of BPA, 2000 mg/L of MLSS and appropriate Synthetic wastewater was added to the Erlenmeyer flasks. The flasks were then shaken on the thermostatic rotary shaker at 125 rpm in the dark. The degradation kinetics of BPA and the effects of initial COD, MLSS and temperature on the aerobic degradation were investigated. Unless otherwise noted, experiments were conducted at the following conditions: 20 °C, pH 7.0, MLSS: 2000 mg/L and the initial COD: 300 mg/L. All the degradation experiments were carried out in duplicate.

At each designed sampling time (0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 8, and 10 h), one Erlenmeyer flask was taken out of the rotary shaker and the mixed liquor was immediately centrifuged at 6000 rpm for 10 min. The supernatant was then filtered through a glass fiber filter (GF/F, 0.45 μ m), and acidified to pH 2 using 1 M HCl. The liquid samples were stored at 4 °C in the dark until solid-phase extraction (SPE) was conducted normally 24 h after centrifugation.

Control samples of BPA without activated sludge were conducted at the same time. No volatile loss was observed during the experiments because of BPA's low Henry's constant ($H = 1.0 \times 10^{-10}$ atm m³/mol) [17]. As BPA is less volatile than water, the volatile loss of BPA during experiments can be neglected.

In this study, we assume that the elimination of BPA in the activated sludge system is achieved by BPA sorption and degradation, and the degraded BPA can be calculated by the following equation:

$$C_{\rm d} = C_0 - C_{\rm e} - q \frac{X}{1000} \tag{7}$$

where C_d is the degraded BPA concentration by activated sludge ($\mu g/L$), C_0 the initial BPA concentration in the wastewater ($\mu g/L$), C_e the BPA concentration remaining in the water phase ($\mu g/L$), q the amount of BPA sorbed on the sludge ($\mu g/kg$) and X is the MLSS concentration in the system (g/L).

The first-order reaction equation was used to describe the degradation rate of BPA:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -kC\tag{8}$$

where *t* is the reaction time (h) and *k* is the first-order reaction constant (h^{-1}) ; *C* is the concentration of residual target compound in the water phase when sorption is ignored. In our experiments, the sorption of BPA on the sludge was significant,

and therefore C represents the residual BPA in the mixed liquor. Eq. (8) can be rewritten in the linear form:

$$\ln\left(\frac{(C_0 - C_d)}{C_0}\right) = -kt\tag{9}$$

From which, the first-order reaction constant *k* can be calculated as the slope of linear regression to BPA data points.

2.5. Sample preparation and analysis

Solid-phase extraction (SPE) was used to extract BPA in wastewater samples. The SupelcleanTM LC-18 cartridges (500 mg, 3 mL) were obtained from Supelco (USA). The extraction procedure was a modification of the method described by Kang and Kondo [18]. The cartridges were previously conditioned by 10 mL methanol and 10 mL deionized water. Water samples of pH 2 passed through the cartridges at a flow rate of 5 mL/min. The cartridges were then washed with 5 mL of a methanol–water (30:70, v/v) solution. After being vacuumdried, cartridges were eluted with 2×5 mL methanol, and the eluates were evaporated to dryness under a gentle stream of nitrogen. Finally, the dried residues were dissolved with 1 mL methanol.

BPA in the extracts was determined by HPLC equipped with fluorescent detector (Varian, USA) and a reversed-phase C-18 column (4.6 mm \times 250 mm, 5 μ m, Agilent, USA). The excitation and emission wavelength were 230 and 290 nm, respectively. The mobile phase was acetonitrile/water (50:50, v/v) and the flow rate was 1 mL/min. The injection volume was 20 μ L.

Soxhlet extraction was applied to determine BPA in the sludge samples. Freeze-dried sludge sample (0.4 g) was soxhletextracted with 100 mL of a solvent mixture of MeOH/CH₂Cl₂ (70:30, v/v) for over 14 h. The extract was concentrated to an approximate volume of 1 mL using a rotary evaporator at 30 °C, which was further dissolved in 200 mL deionized water. The solution was then extracted and measured according to the procedure described in the water samples.

To measure the recovery rate, $2 \mu g/L$ BPA was added to the effluent of the aerobic reactor (the influent was synthetic wastewater without BPA). The samples were prepared and analyzed according to the methods described above. The BPA recovery percentages were in the range of 92–99% (n = 5). The detection limit (S/N = 3) of BPA in the waster samples was 15 ng/L when the volume of extracted sample was 100 mL. The detection limit (S/N = 3) of BPA in the sludge phase was 120 μ g/kg when the extracted dry sludge was 0.4 g.



Fig. 1. Sorption isotherm of BPA on sludge.

3. Results and discussion

3.1. Sorption of BPA on sludge

3.1.1. Sorption equilibrium

The sorption of BPA on the sterilized sludge reached equilibrium quickly (data not shown). At 15 min of contact between BPA and the sludge, the sorption of BPA on the sludge approached 81% of the maximum sorption capacity. From 0.5 to 5 h, only a slight decrease of BPA concentration was observed in the water phase, and the concentration in water did not changed significantly after 5 h. Therefore, the sorption experiments were performed with a contact time of 5 h. When the equilibrium reached at 5 h, the removal efficiency of BPA was about 50%.

3.1.2. Sorption isotherms

The sorption isotherm was shown in Fig. 1. The sorption data were subjected to regression analysis using both Freundlich model and linear model (Table 2). The results indicated that both models fitted well with the experimental data because the correlation coefficients (R^2) were greater than 0.98. Furthermore, in the Freundlich model, 1/n was close to one. Therefore, it is reasonable to assume that partitioning of BPA between the water and sludge phase play a dominant role in BPA sorption on the sludge. This conclusion is consistent with other studies, in which linear isotherm was assumed at low concentration and constant partition coefficient was applied [19].

Our results indicated that K_d and K_{oc} (20 °C) were 336 and 677 L/kg, respectively (Table 2). K_{oc} was comparable to the value (314–1524 L/kg) calculated according to the aqueous solubility and log K_{ow} value of BPA by Howard [17]. Ying et al. [14] claimed that K_{oc} of BPA on the sediment was 778 L/kg. K_{oc} values on different soils determined by Fent et al. [13] were between 636 and 931 L/kg. Ivashechkin et al. [20] indicated that K_{oc} values on different solution of the sediment was 778 L/kg.

Table 2

Freundlich and linear isothermal parameters of BPA sorbed onto the sludge at different temperatures

Temperature (°C)	Freundlich model	Freundlich model			Linear model		
	$K_{\rm f} (\mu {\rm g}^{(1-1/n)} {\rm L}^{1/n} / {\rm kg})$	1/n	R^2	$\overline{K_{\rm d} ({\rm L/kg})}$	$K_{\rm oc}$ (L/kg)	R^2	
10	334	1.04	0.9955	365	736	0.9841	
20	291	1.06	0.9942	336	677	0.9823	
30	220	1.10	0.9919	308	621	0.9959	



Fig. 2. Effect of MLSS concentration on BPA sorption.

ues of BPA on anaerobically digested sludge were in the range of 525–1288 L/kg. K_d values of BPA on activated sludge calculated by Urase and Kikuta were in the range of 217–651 L/kg [10]. Compared to the values in literatures, our values of K_d and K_{oc} were in-line with other values. Ternes et al. [21] suggested that the sorption behavior of organic contaminants in WWTPs can be reasonably predicted by K_d values determined in batch experiments. Since the sorption experiments in the present study were conducted at concentrations close to those found in the raw municipal wastewater (lower $\mu g/L$), the sorption constants measured might be valid for full-scale WWTPs.

3.1.3. Effect of MLSS on BPA sorption

As shown in Fig. 2, the sorption behavior of BPA was apparently influenced by the amount of sorbent in the system. With the increase of MLSS concentration, the amount of sorbed BPA on a unit of sludge decreased. This is because that the increase of suspended solid in the system raised the number of reactive sites available to sorb BPA from solution. Although the amount of sorbed BPA on each gram of sludge decreased due to the competition from the additional available reactive sites, the overall amount of sorbed BPA on solid increased. Therefore, the increase of solid sludge in the solution enhanced the total sorption of BPA by sludge, and benefited the removal of BPA from water.

3.1.4. Effect of temperature on BPA sorption and sorption thermodynamics

The sorption isotherms of BPA at various temperatures (10, 20, and 30 $^{\circ}$ C) were investigated and the corresponding Freundlich and linear isothermal parameters were calculated (Table 2). The results were fitted well to both sorption models, suggesting that partitioning of BPA between water and solid phases played an important role in the system. Data in Table 2 revealed that BPA sorption on sludge decreased with the increase

Table 3 Thermodynamic parameters for the sorption of BPA onto the sludge



Fig. 3. Changes of BPA concentrations in water and solid phases during aerobic degradation.

of temperature, indicating that the sorption was an exothermic reaction. Therefore, increasing temperature benefited BPA desorption from sludge surfaces. The change of 1/n values in the Freundlich model, however, implied some alteration in sorption mechanism due to temperature changes.

A plot of $\ln K_d$ versus 1/T yields a straight line (data not shown). The data fit well to the linear regression Eq. (6) ($R^2 = 0.9988$). The thermodynamic parameters were summarized in Table 3.

The small and negative value of ΔH° confirmed that the sorption process was exothermic and that BPA sorption was mainly physical sorption. The negative values of the free energy ΔG° at different temperatures indicated that the sorption was spontaneous. Because the change of free energy for physical sorption is generally in the range of 0 to -20 kJ/mol [22], the ΔG° values in Table 3 strongly demonstrated that physical partitioning is the dominant process in BPA sorption on sludge. This hypothesis is also supported by the facts that sorption isotherms at different temperatures could be well described by the linear sorption model.

3.2. BPA Degradation by aerobic activated sludge

3.2.1. Degradation kinetics

Fig. 3 shows changes of BPA concentrations in water and sludge phases during the degradation. At the beginning of the reaction, a quick sorption of BPA was observed. About 30% of the spiked BPA was adsorbed by sludge within 15 min, and the quantity of BPA on sludge reached a peak value. Then BPA concentration in both water and sludge phases gradually decreased, and this could be attributed to the degradation of BPA by activated sludge. At 1 h, BPA concentrations in water and sludge phases were $5.26 \,\mu$ g/L and $1832 \,\mu$ g/kg, respectively. At 3 h,

Temperature (°C)	ΔG° (kJ/mol)	ΔS° (J/(mol K))	ΔH° (kJ/mol)
10 20	-13.88 -14.16	27.69	-6.05
30	-14.43		



Fig. 4. Simulation of BPA degradation at 20 $^{\circ}\mathrm{C}$ using first-order reaction equation.

however, the concentrations were only 0.77 μ g/L and 423 μ g/kg. Until the 5th hour, the total elimination efficiency of BPA of the system was almost 100%, in which 98% of BPA was degraded by the activated sludge. Only 177 μ g/kg BPA was found remaining on the sludge. That is to say, most BPA eliminated from water phase was due to the degradation, and only little BPA remained on the sludge at the end of the experiment.

As shown in Fig. 4, BPA degradation data matched well with the first-order reaction Eq. (9) ($R^2 = 0.9924$). Thus, the degradation of BPA by activated sludge was first-order reaction, and the first-order rate constant (k) was $0.804 h^{-1}$. This value was higher than the rate constant ($0.028-0.225 h^{-1}$) determined by Urase and Kikuta [10] using aerobic sludge that was not acclimated to BPA. Whether acclimation or not might be the main reason for the difference because acclimation greatly influenced the degradation behavior of BPA [23].

3.2.2. Effect of initial COD concentration on BPA degradation

The initial COD concentration in the synthetic wastewater was adjusted proportionally with the spiked amount of the organic substrates in Table 1. Fig. 5 shows the effect of initial COD concentration on BPA removal efficiency. At the same reaction time, BPA removal efficiency was higher at low initial COD concentrations. When there was no organic substrate added



Fig. 5. Changes of BPA removal efficiencies at different initial COD concentrations.



Fig. 6. Effect of MLSS on the degradation of BPA.

(COD = 0 mg/L), BPA elimination efficiency at 3 h was close to 100%, while it took 4–5 h to degrade BPA at the initial COD concentration of 300 mg/L. The results suggested that, when easily biodegradable substrates were not available, microorganisms in the activated sludge utilized BPA as carbon source. As organic substrates including glucose, sodium acetate and peptone were more easily degraded by activated sludge than BPA, the presence of these organic substrates in system inevitably slowed down BPA degradation. Urase and Kikuta [10] postulated that a lower initial easily biodegradable substrate content resulted in a higher BPA degradation rate. Therefore, to achieve a high BPA removal efficiency, some pre-elimination of easily biodegradable organic compounds may be necessary.

3.2.3. Effect of MLSS concentration on BPA degradation

The effect of MLSS concentration on BPA degradation was illustrated in Fig. 6. Residual BPA in water phase was lower at a high MLSS concentration than that at a low MLSS concentration. For instance, at 2h, the spiked BPA at MLSS of 3000 mg/L was decreased to $1.07 \mu \text{g/L}$, which was lower than 2.46 and 6.06 μ g/L at the MLSS of 2000 and 1000 mg/L, resulting in the corresponding removal efficiencies as 95%, 88%, and 70%, respectively. These indicate that the removal efficiency of BPA depended markedly upon the levels of MLSS in the reactor. Our sorption results indicated that the elimination efficiency of BPA by sorption on the sludge increased with the increase of MLSS, but the sorbed BPA on each unit weight of sludge decreased. Therefore, there were three possible reasons for higher removal efficiency at higher MLSS. First, a high MLSS concentration means more BPA degradation bacteria and possible quicker degradation rate; second, there is less BPA on per unit weight of sludge in higher MLSS system; third, the sorption removal efficiency was greater at higher MLSS than at lower MLSS. Therefore, it can be concluded that, in addition to sorption, a higher degradation rate contributes the overall high removal efficiency at a higher MLSS concentration.

3.2.4. Effect of temperature on BPA degradation

Temperature had a significant impact on the degradation of BPA over the tested range of 10-30 °C (Fig. 7). Unlike the sorption, the removal efficiency of BPA due to degradation was



Fig. 7. Effect of temperature on the degradation of BPA.

slower at a low temperature than that at a high temperature. The removal efficiencies of BPA at 2 h were 95%, 88%, and 75% at temperatures of 30, 20, and 10 °C, respectively. In another word, it took 10, 6, and 5 h to completely degrade BPA at 10, 20, and 30 °C, respectively. Similar influence of temperature was also reported by Kang and Kondo [24]. They investigated BPA degradation in river, and claimed that, within the river water temperature range of 4–30 °C, the higher the temperature, the faster the BPA degradation.

4. Conclusions

The removal process of BPA in the aerobic activated sludge system was characterized by sorption on activated sludge flocs and subsequent biodegradation. The sorption of BPA on the sterilized sludge could be well described by both Freundlich and linear models. Increasing MLSS concentration or temperature decreased the BPA sorption on the sludge. From sorption thermodynamics and isotherms, it could be inferred that the sorption of BPA onto the sludge was mainly a physical process, in which partitioning played a dominating role. The degradation of BPA followed the first-order reaction, and the first-order degradation rate constant was 0.804 h^{-1} at $20 \degree \text{C}$. The rate of BPA degradation increased with the decrease of initial COD concentration and the increase of MLSS and temperature. Based on the above results, some implications can be obtained to achieve a higher BPA removal efficiency in aerobic activated sludge treatment system: an increase of MLSS or HRT may compensate the adverse impact caused by low temperature in cold area, and improve the BPA removal efficiency. In addition, the elimination of easily biodegradable organic compounds is essential to achieve a high degradation rate of BPA.

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References

 C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O'Block, L.R. Hariis, A review of the environmental fate, effects, and exposures of bisphenol A, Chemosphere 36 (1998) 2149–2173.

- [2] J.H. Kang, F. Kondo, Y. Katayama, Human exposure to bisphenol A, Toxicology 226 (2006) 79–89.
- [3] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other compounds in US streams, 1999–2000: a national reconnaissance, Environ. Sci. Technol. 36 (2002) 1202–1211.
- [4] X.L. Jin, G.B. Jiang, G.L. Huang, J.F. Liu, Q.F. Zhou, Determination of 4-tert-octylphenol, 4-nonylphenol and bisphenol A in surface waters from the Haihe River in Tianjin by gas chromatography-mass spectrometry with selected ion monitoring, Chemosphere 56 (2004) 1113– 1119.
- [5] N. Ben-Jonathan, R. Steinmetz, Xenoestrogens: the emerging story of bisphenol A, Trends Endocrinol. Metab. 9 (1998) 124–128.
- [6] M. Fürhacker, S. Scharf, H. Weber, Bisphenol A: emissions from point sources, Chemosphere 41 (2004) 751–756.
- [7] W. Körner, U. Bolz, W. Süßmuth, Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany, Chemosphere 40 (2000) 1131–1142.
- [8] H.B. Lee, T.E. Peart, Bisphenol A contamination in Canadian municipal and industrial wastewater and sludge samples, Water Quality Res. J. Canada 35 (2000) 283–289.
- [9] M. Nasu, M. Goto, H. Kato, Y. Oshima, H. Tanaka, Study on endocrine disrupting chemicals in wastewater treatment plants, Water Sci. Technol. 43 (2001) 101–108.
- [10] T. Urase, T. Kikuta, Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process, Water Res. 39 (2005) 1289–1300.
- [11] U.T. Berg, N. Nyholm, Biodegradability simulation studies in semicontinuous activated sludge reactors with low (μ g/L range) and standard (ppm range) chemical concentrations, Chemosphere 33 (1996) 711– 735.
- [12] G.M. Zeng, C. Zhang, G.H. Huang, J. Yu, Q. Wang, J.B. Li, B.D. Xi, H.L. Liu, Adsorption behavior of bisphenol A on sediments in Xiangjiang River, Central-south China, Chemosphere 65 (2006) 1490–1499.
- [13] G. Fent, W.J. Hein, M.J. Moendel, R. Kubiak, Fate of ¹⁴C-bisphenol A in soils, Chemosphere 51 (2003) 735–746.
- [14] G.G. Ying, R.S. Kookana, P. Dillon, Sorption and degradation of selected five endocrine disrupting chemicals in aquifer material, Water Res. 37 (2003) 3785–3791.
- [15] X. Wang, C.P.L. Grady Jr., Comparison of biosorption isotherms for din-butyl phthalate by live and dead bacteria, Water Res. 28 (1994) 1247– 1251.
- [16] H. Koyuncu, A.R. Kul, N. Yildiz, A. Çalımlı, H. Ceylan, Equilibrium and kinetic studies for sorption of 3-methoxybenzaldehyde on activated kaolinites, J. Hazard. Mater. 141 (2007) 128–139.
- [17] P.H. Howard, Handbook of environmental fate and exposure data, Vol. 1, Lewis Publishers, Chelsea, 1989.
- [18] J.H. Kang, F. Kondo, Bisphenol A degradation in seawater is different from that in river water, Chemosphere 60 (2005) 1288–1292.
- [19] G. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, V. Barthès, M. Krimissa, Sorption isotherms: a review on physical bases, modeling and measurement, Appl. Geochem. 22 (2007) 249–275.
- [20] P. Ivashechkin, P.F.-X. Corvini, M. Dohmann, Behaviour of endocrine disrupting chemicals during the treatment of municipal sewage sludge, Water Sci. Technol. 50 (2004) 133–140.
- [21] T.A. Ternes, N. Herrmann, M. Bonerz, T. Knacker, H. Siegrist, A. Joss, A rapid method to measure the solid–water distribution coefficient (K_d) for pharmaceuticals and musk fragrances in sewage sludge, Water Res. 38 (2004) 4075–4084.
- [22] Y. Wang, Y. Mu, Q.B. Zhao, H.Q. Yu, Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge, Sep. Purif. Technol. 50 (2006) 1–7.
- [23] M. Ike, C.S. Jin, M. Fujita, Biodegradation of bisphenol A in the aquatic environment, Water Sci. Technol. 42 (2000) 31–38.
- [24] J.H. Kang, F. Kondo, Effects of bacterial counts and temperature on the biodegradation of bisphenol A in river water, Chemosphere 49 (2002) 493–498.