Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.803663

52 (2014) 4388–4394
June

Taylor & Francis
Taylor & Francis Group

Cationic surfactant hemimicelle on alginate gel for removing bisphenol A from aqueous solution

Jun Zhu, Miaomiao Dai, Suoju He, Qiumei Lai, Renmin Gong*

School of Life Science, Anhui Normal University, Wuhu 241000, P.R. China
Tel. +86 5535991085; email: renmin.gong@yahoo.com

Received 20 March 2012; Accepted 30 April 2013

ABSTRACT

In this paper, alginate gel (AG) was prepared by cross-linking sodium alginate with calcium ion. By adding cationic surfactant cetyl trimethyl ammonium bromide (CTAB) as sorption medium, the bisphenol A (BPA) sorption from aqueous solution onto AG was investigated. The BPA removal was found to be dependent on initial pH, AG dose, CTAB concentration, BPA concentration, contact time, and temperature. The isothermal data of BPA sorption on AG conformed well to the Langmuir model, and the maximum sorption capacity (Q_m) of AG for BPA was 30.96 mg/g. The BPA sorption process could be described by the pseudo-second-order rate kinetic model. The thermodynamic study indicated that the BPA sorption process was spontaneous and exothermic. The results in this research confirmed that the AG could effectively remove BPA from aqueous solution in presence of the CTAB. The following sorption mechanism was proposed. Firstly, the negatively charged AG sorbed CTAB to form hemimicelle, then BPA was sorbed on hemimicelle by hydrophobic interaction.

Keywords: Cationic surfactant; Hemimicelle; Alginate gel; Bisphenol A; Sorption

1. Introduction

The endocrine system is a group of glands that work together and secrete many types of different hormones regulating various important functions in humans and many other animals. Endocrine disrupting compounds (EDCs) are exogenous substances that act like hormones in the endocrine system and disrupt the physiologic function of endogenous hormones. Among various problems caused by EDCs, the pollution of phenolic EDCs in environmental water has aroused the public concerns as these contaminants were frequently detected in different water sources in recent years [1,2]. Bisphenol A (BPA), a phenolic EDC, has been widely used as the monomeric substance for the production of polycarbonate and epoxy-phenolic resins, and as the stabilizer or antioxidant for many types of plastics [3]. So, it is inevitably released into the aquatic environment through various routes. The potential adverse effects of BPA on human health and reproductive biology include breast and prostate cancers, sperm count reduction, abnormal penile/urethra development in males, early sexual maturation in females, neurobehavioral problems, prevalence of obesity, type 2 diabetes, and immunodeficiency. These adverse effects of BPA on human health induce urgent need for developing the effective technique to eliminate BPA from aquatic environment.

---

*Corresponding author.

A number of methods such as phytoremediation [4], biodegradation [5–7], electrochemical process [8], ozonation [9], chemical oxidation [10], enzymatic oxidation [11], photooxidation [12], ultrasonic degradation [13], solvent extraction [14], membrane filtration [15], and sorption [16] have been employed to eliminate BPA from wastewater. Recently, a few materials had been used as sorbents for removing BPA from aqueous solution, which included aquifer material [17], chitosan-bearing β-cyclodextrin [18], polysulfone bead [19], mineral [20], hydrophobic zeolite [21], carbon nanomaterial [22], activated carbon [23], and molecularly imprinted polymer [24], hybrid mesoporous silicas [25], modified peat [26], and lignin [27].

Alginic acid is a naturally occurring hydrophilic colloidal polysaccharide obtained from the various species of marine brown alga. It is a linear copolymer consisting mainly of residues of β-1,4-linked D-mannuronic acid and α-1,4-linked L-glucuronic acid. These monomers are often arranged in a nonregular and blockwise fashion along the chain. Sodium alginate, a water soluble salt of alginic acid, exhibits a sol-gel transition when simply submitted to modification of its ionic environment, e.g. substitution of monovalent sodium ion by divalent or polyvalent metal ions such as calcium, copper, zinc, and aluminum.

In the present work, a new sorption mechanism of hemimicelles for removing hydrophobic environmental pollutants from aqueous solution was proposed. The sodium alginate was cross-linked by calcium ion for preparing alginate gel (AG) as sorbent. The cationic surfactant cetyl trimethyl ammonium bromide (CTAB) was sorbed on oppositely charged AG through coulombic attraction to form hemimicelles at certain concentration level called critical hemimicellar concentration (CHC), and then BPA was sorbed on hemimicelles of AG through hydrophobic interaction between the hydrophobic moieties of surfactant on hemimicelles and aromatic alkyl groups of BPA. The proposed hydrophobic sorption mechanism had been applied to remove BPA from aqueous solution in a batch system.

2. Experimental

2.1. Materials and reagents

Sodium alginate and CTAB were purchased from Sigma Chemical Co., USA and Amresco Inc., USA, respectively. The standard BPA (Sinopharm Chemical Reagent Shanghai Co., Ltd., China) stock solution (200 mg/L) was obtained by dissolving 0.100 g of solid BPA in 5 mL of ethanol, then diluting in 500 mL volumetric flask with deionized water and stored under refrigeration. The working solutions (pH 6.94) were prepared by diluting the stock solution in accurate proportions to different initial concentrations. All other chemicals were of analytical grade and used without further purification.

2.2. Preparation of alginate gel

AG beads were prepared by dropwise addition of 2% of viscous sodium alginate solution (w/v) to 3% calcium chloride solution (w/v) in a stirrer. After 1 h stirring, the resulting gel beads were stored in the calcium chloride solution for 1 h at room temperature. Na-alginate reacts with calcium chloride to form beads and cross-linked Ca-alginate was formed. During the process, the water soluble sodium alginate was converted into water insoluble calcium AG beads. The resultant gel beads were washed with deionized water to remove calcium chloride from the gel surfaces and collected by filtration. The gel beads were then dried at room temperature until no weight change was observed.

2.3. BPA sorption experiments

Sorption experiments were carried out in a rotary shaker at 150 rpm and ambient temperature (except the experiments of temperature effect) using 250 mL shaking flasks containing 100 mL of BPA working solutions with known final concentration, desired CTAB concentration, and initial pH values. The initial pH values of BPA working solutions were adjusted with diluted HNO_3 or NaOH using a pH meter. Different dose of AG was added into each flask, and then the flasks were sealed up to prevent volume change of the solutions during the experiment. After shaking the flasks for predetermined time intervals, the samples were separated and the residual concentration of BPA in solutions was estimated by HPLC under the following conditions: column, TSKgel ODS-80Ts 4.6 mm i.d. × 250 mm (Tosoh Corp., Japan); eluent, methanol/distilled water (7:3, v/v); flow rate, 1 mL/min; temperature, 40℃; and eluent detection at 270 nm. The amount of BPA sorbed on AG was calculated by the mass balance equation.

3. Results and discussion

3.1. Influence of solution pH

The influence of solution pH on BPA sorption was shown in Fig. 1. The BPA sorption percentage on AG increased as the initial pH was increased from 2 to 3, then kept maximum value in the pH range of 3–8,

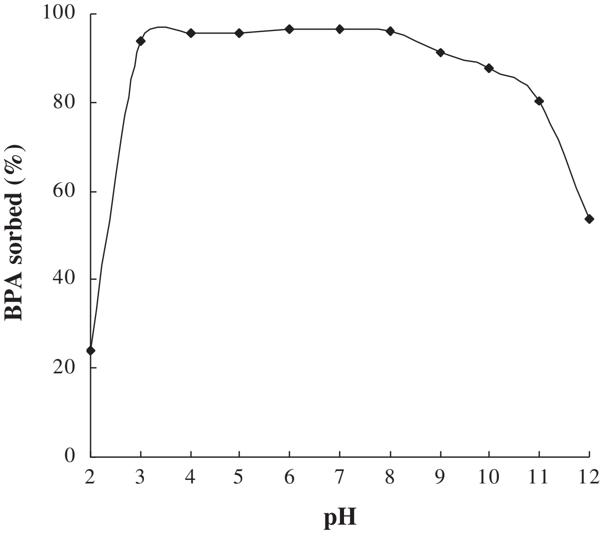

Fig. 1. Influence of initial pH on removal of BPA by AG (BPA concentration: 50 mg/L; AG dose: 2.5 g/L; CTAB concentration: 450 mg/L; contact time: 13 h).

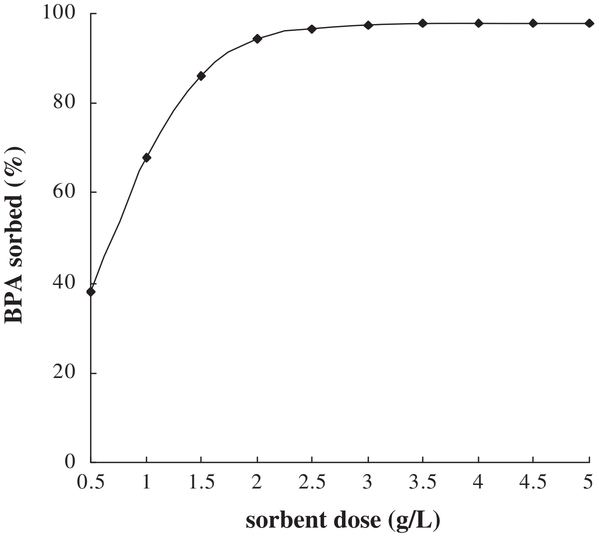

Fig. 2. Effect of sorbent dose on removal of BPA by AG (BPA concentration: 50 mg/L; CTAB concentration: 450 mg/L; contact time: 13 h; pH: 6.94).

and decreased as the pH was continually increased from 8 to 12.

When pH < 3, the formation of CTAB hemimicelle decreased because of protonation of negative charged AG, the removal of BPA decreased. When pH > 8, the hydrophobic interaction between the hydrophobic moieties of CTAB on the hemimicelle and aromatic alkyl groups of BPA decreased because of deprotonation of BPA, together with the electrostatic repulsion between BPA anion and negative charged AG, the removal of BPA decreased.

3.2. Effect of sorbent dose

The effect of sorbent dose on BPA sorption is presented in Fig. 2. When AG dose was increased from 0.5 to 2.5 g/L, the BPA sorption percentage on AG increased from 38.30 to 96.51%. After that, the BPA sorption ratio on AG held almost no variety. Increase in the BPA sorption ratio with sorbent dose could be imputed to increased sorbent surface area and availability of more sorption sites.

3.3. Influence of CTAB concentration

The BPA removed from aqueous solution by AG was based on the hydrophobic sorption mechanism of hemimicelles. At certain concentration level called CHC, the cationic CTAB was sorbed on oppositely charged AG through coulombic attraction and formed hemimicelles, and then BPA was sorbed on AG through hydrophobic interaction between the hydrophobic moieties of CTAB hemimicelles on AG and aromatic alkyl groups of BPA.

As the intermediary of BPA sorbed on AG, the influence of CTAB concentration on BPA sorption is shown in Fig. 3. When the CTAB concentration was less than 100 mg/L, any BPA sorption could not be observed. This result was consistent with our expectation. Along with the increase of CTAB concentration from 150 to 450 mg/L, the BPA sorption percentage on AG increased from 32.41 to 96.66%. But with further

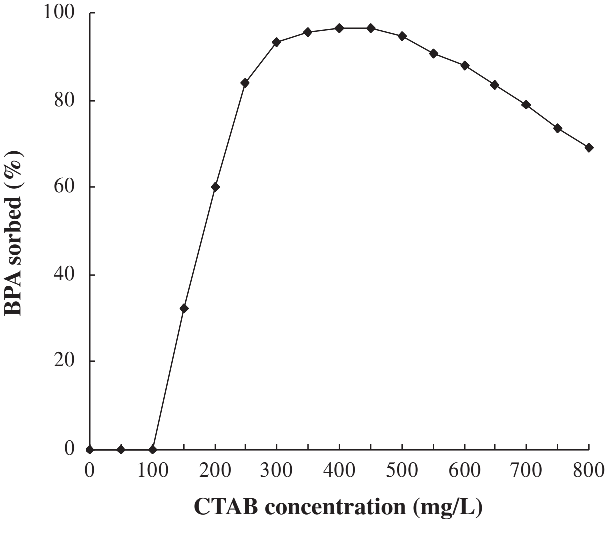

Fig. 3. Influence of CTAB concentration on removal of BPA by AG (BPA concentration: 50 mg/L; AG dose: 2.5 g/L; contact time: 13 h; pH: 6.94).

increase of CTAB concentration up to 800 mg/L, the BPA sorption percentage on AG obviously decreased. The obvious decrease of BPA sorption percentage with increase of CTAB concentration could be attributed to the formation of CTAB admicelle on AG and CTAB micelle in solution. The BPA molecules in solution cannot be sorbed by CTAB admicelle on AG and CTAB micelle in solution will hinder the sorption of BPA on sorbent.

3.4. Effect of BPA concentration and sorption isotherm

The effect of BPA concentration on its sorption is presented in Fig. 4. Over the 10–50 mg/L of BPA concentration range, its removal ratio on AG of 2.5 g/L exceeded 96%. With further increase of BPA concentration up to 100 mg/L, the BPA sorption percentage on AG obviously decreased. The decrease of BPA sorption percentage could be imputed to the lack of available active sites on AG required for the high BPA concentration.

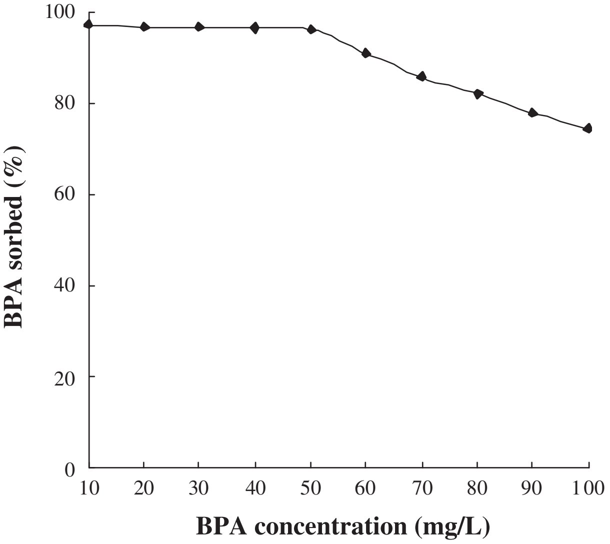

Fig. 4. Effect of BPA concentration on its removal by AG (AG dose: 2.5 g/L; CTAB concentration: 450 mg/L; contact time: 13 h; pH: 6.94).

The following Langmuir and Freundlich equations were employed to study the sorption isotherm of BPA on AG:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \tag{1}$$

$$\ln q_e = \ln K + (1/n)\ln C_e \tag{2}$$

where C_e (mg/L) is the concentration of BPA solution at equilibrium, q_e (mg/g) is the amount of sorbed BPA at equilibrium. In Langmuir equation, Q_m is the maximum sorption capacity and a is Langmuir constant. In Freundlich equation, K and n are empirical constants.

The simulated Langmuir and Freundlich equations based on the experimental data in Fig. 4, and the values of parameters and correlation coefficients are shown in Table 1. The values of correlation coefficient in Table 1 indicate that the sorption isotherm of BPA on AG only followed the Langmuir model. The maximum sorption capacity (Q_m) of AG for BPA obtained from the simulated Langmuir equation was 30.96 mg/g. The sorption capacities (Q_m) of some sorbents for BPA are compared in Table 2.

3.5. Influence of contact time and sorption kinetics

The influence of contact time on BPA sorption is shown in Fig. 5. It can be seen from Fig. 5 that the BPA sorption velocity gradually declined with the progression of sorption, and then the sorption reached saturation at about 13 h.

The following pseudo-first-order and pseudo-second-order rate equations were used to study the kinetic model of BPA sorption:

$$\ln(q_e - q_e) = \ln q_e - k_{ad}\, t \tag{3}$$

$$t/q_t = 1/k_{ad}{q_e}^2 + t/q_e \tag{4}$$

where q_e and q_t refer to the amount of sorbed BPA at equilibrium and time t (min), respectively (mg/g), and k_{ad} is the rate constant.

Table 1
The isotherm equations and parameters of BPA sorption on AG

Sorbate	Langmuir			Freundlich		
	$C_e/q_e = 0.0323C_e + 0.0595$			$\ln q_e = 0.3838\ln C_e + 2.3214$		
	Q_m(mg/g)	a (L/mg)	R^2	K (mg/g)(mg/L)^n	n	R^2
BPA	30.96	0.5429	0.9958	10.19	2.6055	0.8641

Table 2
The sorption capacities (Q_m) of various sorbents for BPA

Sorbate	Sorbent	Q_m (mg/g)	Reference
BPA	Chitosan-bearing β-cyclodextrin	139	[18]
	Hydrophobic zeolite	111.11	[21]
	AG	30.96	Present study
	HTAB-modified peat	29.15	[26]
	Unmodified peat	15.97	[26]

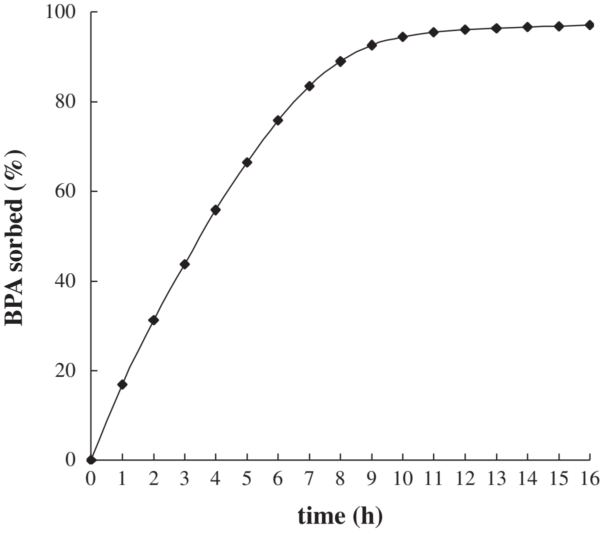

Fig. 5. The kinetic curve of BPA sorption on AG (BPA concentration: 50 mg/l; AG dose: 2.5 g/L; CTAB concentration: 450 mg/L; pH: 6.94).

The simulated pseudo-first-order and pseudo-second-order rate equations based on the experimental data in Fig. 5, and the values of parameters and correlation coefficients are shown in Table 3. The correlation coefficients in Table 2 indicate that the kinetics of BPA sorbed on AG conformed to pseudo-second-order rate equation better than pseudo-first-order rate equation.

3.6. Effect of temperature and sorption thermodynamics

The effect of temperature on BPA sorption was studied at 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15 K. The thermodynamic parameters, ΔH° and ΔS°, were obtained from the following Van't Hoff equation:

$$\ln(q_e/C_e) = \Delta S^\circ/R - \Delta H^\circ/RT \tag{5}$$

where q_e/C_e is the equilibrium constant (mL/g), ΔS° is standard entropy (J/mol K), ΔH° is standard enthalpy (J/mol), T is the absolute temperature (K), and R is the gas constant (8.314 J/mol K). From Fig. 6, the ΔH° and ΔS° values can be calculated from the slope ($-\Delta H^\circ$/R) and intercept (ΔS°/R) of the linear plot of ln (q_e/C_e) vs. $1/T$.

The thermodynamic parameter, ΔG°, was calculated from the following Gibbs–Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

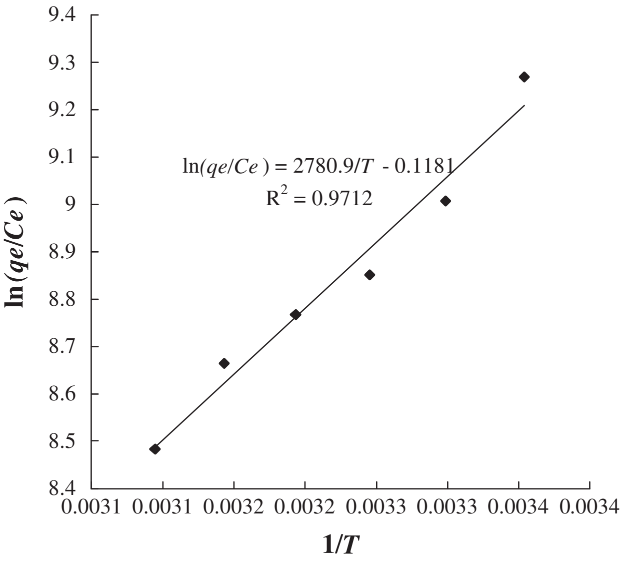

Fig. 6. The thermodynamic plot of BPA sorption on AG (BPA concentration: 50 mg/L; AG dose: 2.5 g/L; CTAB concentration: 450 mg/L; contact time: 13 h; pH: 6.94).

Table 3
The kinetic equations and parameters of BPA sorption on AG

Sorbate	Pseudo-first-order			Pseudo-second-order		
	$\ln(q_e - q_t) = -0.4066\,t + 3.5433$			$t/q_t = 0.2635 + 0.0243\,t$		
	q_e (mg/g)	k_{ad} (1/min)	R^2	q_e (mg/g)	k_{ad} (g/mg min)	R^2
BPA	34.581	0.4066	0.9539	41.152	0.0022	0.9752

Table 4
The thermodynamic parameters of BPA sorption on AG

Sorbate	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)					
			298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
BPA	−23.120	−0.9819	−22.828	−22.823	−22.818	−22.813	−22.808	−22.803

where ΔG° is the standard free energy (kJ/mol). The ΔG° values under different temperatures as well as ΔH° and ΔS° values are presented in Table 4. The negative values of ΔG° and ΔH° indicated that the BPA sorption were spontaneous and exothermic. Lower temperatures were favorable for the sorption process. It was speculated that the thermal movement of molecules could weaken the hydrophobic interaction between the linear hydrocarbon chain of CTAB on hemimicelle and aromatic alkyl groups of BPA, maybe high temperature also affected the formation of hemimicelle. So BPA sorption decreases at high temperature.

4. Conclusion

This work confirmed that AG could effectively remove BPA from the aqueous solution containing cationic surfactant. The BPA sorption percentage was affected by initial pH, AG dose, CTAB concentration, BPA concentration, contact time, and temperature. The maximum value of BPA sorption appeared in the pH range of 3–8. The isothermal data of BPA sorbed on AG conformed to the Langmuir model. Based on the simulated Langmuir equation, the sorption capacity (Q_m) of AG for BPA was 30.96 mg/g. The kinetics of BPA sorbed on AG followed the pseudo-second-order rate equation better than the pseudo-first-order rate equation. The thermodynamic study suggested that the BPA sorption process was spontaneous and exothermic.

Acknowledgments

The authors wish to express their thanks to the Key Laboratory of Bioresource Protection and Utilization of Anhui Province, the Key Laboratory of Biotic Environment and Ecological Safety of Anhui Province, and the Key Science Research Item of Anhui Normal University for the financial supports.

References

[1] C. Desbrow, E.J. Routledge, G.C. Brighty, J.P. Sumpter, M. Waldock, Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and *in vitro* biological screening, Environ. Sci. Technol. 32 (1998) 1549–1558.

[2] A. Laganà, A. Bacaloni, I.D. Leva, A. Faberi, G. Fago, A. Marino, Analytical methodologies for determining the occurrence of endocrine disrupting chemicals in sewage treatment plants and natural waters, Anal. Chim. Acta 501 (2004) 79–88.

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

[4] M.I. Noureddin, T. Furumoto, Y. Ishida, H. Fukui, Absorption and metabolism of bisphenol A, a possible endocrine disruptor, in the aquatic edible plant, water convolvulus (*Ipomoea aquatica*), Biosci. Biotech. Biochem. 68 (2004) 1398–1402.

[5] W. Chai, H. Sakamaki, S. Kitanaka, M. Saito, C.A. Horiuchi, Biodegradation of bisphenol A by cultured cells of *Caragana chamlagu*, Biosci. Biotech. Biochem. 67 (2003) 218–220.

[6] S.-M. Lee, B.-W. Koo, J.-W. Choi, D.-H. Choi, B.-S. An, E.-B. Jeung, I.-G. Choi, Degradation of bisphenol A by white rot fungi, *Stereum hirsutum* and *Heterobasidium insulare*, and reduction of its estrogenic activity, Biol. Pharm. Bull. 28 (2005) 201–207.

[7] K. Sakai, H. Yamanaka, K. Moriyoski, T. Ohmoto, T. Ohe, Biodegradation of bisphenol A and related compounds by *Sphingomonas* sp. strain BP-7 isolated from seawater, Biosci. Biotech. Biochem. 71 (2007) 51–57.

[8] H. Kuramitza, M. Matsushita, S. Tanaka, Electrochemical removal of bisphenol A based on the anodic polymerization using a column type carbon fiber electrode, Water Res. 38 (2004) 2331–2338.

[9] M. Deborde, S. Rabouan, P. Mazellier, J.-P. Duguet, B. Legube, Oxidation of bisphenol A by ozone in aqueous solution, Water Res. 42 (2008) 4299–4308.

[10] M. Yoshida, H. Ono, Y. Mori, Y. Chuda, K. Onishi, Oxidation of bisphenol A and related compounds, Biosci. Biotech. Biochem. 65 (2001) 1444–1446.

[11] Y.J. Xuan, Y. Endo, K. Fujimoto, Oxidative degradation of bisphenol A by crude enzyme prepared from potato, J. Agr. Food Chem. 50 (2002) 6575–6578.

[12] D. Zhou, F. Wu, N. Deng, W. Xiang, Photooxidation of bisphenol A (BPA) in water in the presence of ferric and carboxylate salts, Water Res. 38 (2004) 4107–4116.

[13] J.-S. Park, N. Her, Y. Yoon, Ultrasonic degradation of bisphenol A, 17b-estradiol, and 17a-ethinyl estradiol in aqueous solution, Desalin. Water Treat. 30 (2011) 300–309.

[14] J. Fan, Y. Fan, Y. Pei, K. Wu, J. Wang, M. Fan, Solvent extraction of selected endocrine-disrupting phenols using ionic liquids, Sep. Purif. Technol. 61 (2008) 324–331.

[15] Y. Zhang, C. Causserand, P. Aimar, J.P. Cravedi, Removal of bisphenol A by a nanofiltration membrane in view of drinking water production, Water Res. 40 (2006) 3793–3799.

[16] Y. Li, N. Li, D. Chen, X. Wang, Z. Xu, D. Dong, Bisphenol A adsorption onto metals oxides and organic materials in the natural surface coatings samples (NSCSs) and surficial sediments (SSs): Inhibition for the importance of Mn oxides, Water Air Soil Pollut. 196 (2009) 41–49.

[17] 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.

[18] N. Aoki, R. Arai, K. Hattori, Improved synthesis of chitosan-bearing β-cyclodextrin and its adsorption behavior towards bisphenol A and 4-nonylphenol, J. Incl. Phenom. Macro. 50 (2004) 115–120.

[19] C. Zhao, Q. Wei, K. Yang, X. Liu, M. Nomizu, N. Nishi, Preparation of porous polysulfone beads for selective removal of endocrine disruptors, Sep. Purif. Technol. 40 (2004) 297–302.

[20] M. Shareef, M.J. Angove, J.D. Wells, B.B. Johnson, Sorption of bisphenol A, 17α-ethynylestradiol and estrone to mineral surfaces, J. Colloid Interf. Sci. 297 (2006) 62–69.

[21] W.-T. Tsai, H.-C. Hsu, T.-Y. Su, K.-Y. Lin, C.-M. Lin, Adsorption characteristics of bisphenol-A in aqueous solutions onto hydrophobic zeolite, J. Colloid Interf. Sci. 299 (2006) 513–519.

[22] B. Pan, D. Lin, H. Mashayekhi, B. Xing, Adsorption and hysteresis of bisphenol A and 17α-ethinyl estradiol on carbon nanomaterials, Environ. Sci. Technol. 42 (2008) 5480–5485.

[23] G. Liu, J. Ma, X. Li, Q. Qin, Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments, J. Hazard. Mater. 164 (2009) 1275–1280.

[24] W.F. Zhao, B.H. Fang, N. Li, S.Q. Nie, Q. Wei, C.S. Zhao, Fabrication of pH-responsive molecularly imprinted polyethersulfone particles for bisphenol-A uptake, J. Appl. Polym. Sci. 113 (2009) 916–921.

[25] Y.-H. Kim, B. Lee, K.-H. Choo, S.-J. Choi, Selective adsorption of bisphenol A by organic–inorganic hybrid mesoporous silicas, Micropor. Mesopor. Mater. 138 (2011) 184–190.

[26] Y. Zhou, L. Chen, P. Lu, X. Tang, J. Lu, Removal of bisphenol A from aqueous solution using modified fibric peat as a novel biosorbent, Sep. Purif. Technol. 81 (2011) 184–190.

[27] W. Han, L. Luo, S. Zhang, Adsorption of bisphenol A on lignin: Effects of solution chemistry, Int. J. Environ. Sci. Technol. 9 (2012) 543–548.