Title	Adsorption modeling by two sites Langmuir type isotherm for adsorption of bisphenol-A and diethyl phthalate onto activated carbon in single and binary system
Author(s)	Maruyama, Hideo; Seki, Hideshi
Citation	Separation Science and Technology, 57(10), 1535-1542 https://doi.org/10.1080/01496395.2021.1995426
Issue Date	2021-11-01
Doc URL	http://hdl.handle.net/2115/87059
Rights	This is an Accepted Manuscript of an article published by Taylor & Francis in Separation Science and Technology on 2021, available online: https://www.tandfonline.com/ 10.1080/01496395.2021.1995426.
Type	article (author version)
File Information	manuscript_20211110.pdf

Adsorption modeling by two sites Langmuir type isotherm for adsorption of bisphenol-A and diethyl phthalate onto activated carbon in single and binary system

Hideo MARUYAMA[*] and Hideshi SEKI

Division of Marine Bioresources, Graduate School of Fisheries Sciences,
Hokkaido University, Minato-cho 3-1-1, Hakodate 041-8611, Japan

[*] Corresponding author.

E–mail address: maruyama@fish.hokudai.ac.jp (H. Maruyama)

Abstract

Adsorption of bisphenol-A (BPA) and diethyl phthalate (DEP) onto activated carbon has been studied. The experimental adsorption data is reasonably well fitted by a two site Langmuir isotherm model. The estimated two equilibrium adsorption constants were almost the same even though the adsorbates were different. This suggested that the existence of two types of adsorption sites with different equilibrium adsorption constants for strong and weak sites on the present activated carbon surface. The equilibrium adsorption constant of strong site was 130 times larger than that of weak site, and the saturated adsorption density of weak site was 2.6 and 3.6 times larger than that of strong site for BPA and DEP, respectively. In addition, adsorption experiments of the binary system have also been carried out. Based on suggesting two type sites, two models, competitive adsorption or non-competitive adsorption models, were attempted to apply to the experimental results. Judging from the model consideration, the non-competitive model could describe well the adsorption isotherm in the binary system. Compared with the single system, in the binary system, the equilibrium adsorption constants were almost the same, but the saturated adsorption densities were 10% to 30% lower than that of the single system.

Keywords: adsorption; bisphenol-A; diethyl phthalate; activated carbon; two site Langmuir isotherm

1. Introduction

Some substances have been reported to affect the aquatic environment, such as nitrogenous compounds, ammonia and nitric acid, aromatic compounds, phenol, divalent heavy metal ions, and organochlorine compounds, and methods to remove or decompose these substances and to control histamine-producing bacteria have been proposed (Azari et al., 2014; Naghan et al., 2015; Ahmadi et al., 2016; Azari et al., 2016; Rahmani et al., 2019).

In recent two decades, among them, the influence of environmental distributed chemicals, so-called endocrine disrupting chemicals (EDCs), on humans, vertebrates, etc. have been reported. Among EDCs, bisphenol-A is well-known to influence hormonal signals and have an irreversible effect on the development of the reproductive organs. Especially, many reports of these influences on fish have appeared in the literature (Sohoni et al., 2001; Belfroid et al., 2002; Kashiwada et al., 2002; Baek et al., 2003; Ohkubo et al., 2003; Nakada et al., 2004; Lahnsteiner et al., 2005; Nagae et al., 2005; Sumpter and Johnson, 2005). Fish and shellfish are important to humans, not only as food or protein resources but also as resources of physiologically active and bioactive substances.

In the environmental aqueous phase, the concentration of these EDCs has been very low level, for example, the level was extremely lower than a few ppb due to their low solubility to water. For this reason, it is so difficult to remove these EDCs from natural aqueous environments. On the other hand, in industrial wastewater, the concentration level of EDCs is higher than the ppm-level. Therefore, it is important to remove EDCs in the industrial treatment stage.

For conservation and restoration of the aqueous environments or aquaculture systems, attempts have been made to remove these substances. For this purpose, several techniques have been attempted and developed (i.e., adsorption method using solid adsorbents (Nakanishi et al., 2002; Emmerik et al., 2003; Kubo et al., 2005; Tsue et al., 2005; Shareef et al., 2006), degradation using ozone and ultraviolet light irradiation (Irmak et al., 2005) degradation by catalyzed or enzymatic methods (Coleman et al., 2005; Modaressi et al., 2005) degradation by ultrasonic sound irradiation (Abderrazik et al., 2005) and so on). However, it is reported that the degraded substances can also affect several animals or fishes as same as EDCs. For preventing the degradation of EDCs, EDCs should be removed to keep the natural chemical structure of EDCs without degradation. For this purpose, the adsorption technique could be employed to remove EDCs from the aqueous phase due to simple operation at ease. Adsorption of EDCs onto objective adsorbents has been studied with several adsorbents. Several kinds of adsorbents have been attempted to remove EDCs from the aqueous phase. Among them, activated carbon has been used as a typical general adsorbent due to getting at ease, inexpensive, and so on. Many studies on the adsorption of EDCs onto activated carbon have been carried out in terms of especially adsorption kinetics and adsorption isotherm (Toledo et al., 2005; Hohan et al., 2007; Kumar and Namasivayam, 2014; Sudhakar and Srivastava, 2016; Martín-Lara et al., 2020). However, most of these studies have only reported which are the well-established adsorption kinetics models or adsorption isotherms equations agreed well with the experimental results. This method is good for solving particular problems, but it lacks the potential for development, such as proposing a new adsorption mechanism. Moreover, these previously reported studies have only dealt with a single system of EDSs, but also there have been few reports about adsorption mechanism and adsorption modeling. It is so important for adsorptive separation process design and development to know and propose the adsorption mechanism of the subjective substances from the viewpoint of chemical engineering aspect.

In this study, we conducted batch adsorption experiments by using bisphenol-A and diethyl phthalate as model adsorbate compounds of EDCs and a commercial activated carbon as an adsorbent. The adsorption experiments were conducted in each single and binary system, respectively. The adsorption behavior and adsorption mechanism are discussed in the present study.

2. Materials and Methods

2.1. Chemicals

Bisphenol-A (BPA) and diethyl phthalate (DEP) were purchased from Kanto Chemical Inc. (Japan). Each 5.0×10^{-4} M solution was prepared as a mother solution. By diluting this solution, the concentration of BPA or DEP was adjusted to the desired concentration for the batch adsorption experiment. Acetonitrile was purchased from Wako Pure Chemical Industries (Japan) as a mobile phase media of high-performance liquid chromatography to determine BPA and DEP. All chemicals were used in this study without further purification.

2.2. Activated carbon as adsorbent

Activated carbon powder (AC) was purchased from Wako Pure Chemical Industries (Japan). AC powder was prepared by the following procedure. The quartz sand was washed with distilled water and was dried at 60°C for 48 h. According to the information from the supplier, the specific surface area and the pore volume of AC were 1530 m^2/g and 1.32 cm^3/g, respectively, and the diameter (d) distribution of AC was as follows: $d < 49$ μm (ca. 55-75 %); $49 \le d \le 150$ μm (ca. 20-40 %); $d > 150$ μm (ca 10 %).

2.3. Procedure of batch adsorption experiment

A desired amount of AC was taken into a 300 mL flask, then ca. 100 mL of distilled water was also poured into the flask. Then, the flask was heated until boiling for 2 min to remove air within pores of AC. After this, the flask was set at room temperature for cooling. After thermal equilibrium at room temperature, the flask and a stock bottle of the mother solution (BPA or DEP) were set in a 30 °C water bath. The AC suspension was stirred by using a magnetic stirrer (300 rpm). By adding the desired amount of the mother solution and distilled water, the liquid volume within the flask was adjusted to 300 mL, and the adsorption experiment was started. The solution was also stirred throughout until adsorption equilibrium. In all experiments, 24 hours was acquired to reach the adsorption equilibrium state. By varying the initial concentration of BPA or DEP, the batch adsorption experiment was repeated to obtain the adsorption isotherm of BPA or DEP. In the case of a binary system, a mother solution of BPA-DEP mixture was prepared and was used for batch adsorption experiments. In all binary adsorption experiments, the molar ratio of BPA and DEP in the initial concentration was employed as 1:1. The amount adsorbed of BPA or DEP was determined from the difference between the initial and the equilibrium concentration of BPA or DEP. The concentration of BPA or DEP was determined by using HPLC (130A Separation System, Applied Biosystems) with a UV detector (225 nm).

3. Results and Discussion

3.1. Adsorption isotherm of BPA and DEP in a single system

The adsorption isotherm of BPA and DEP are shown in Fig. 1. By comparing the amount adsorbed of both EDCs, the amount adsorbed of BPA was slightly larger than that of DEP in the experimental range. As seen in Fig. 1, for example, by comparison at same equilibrium concentration, C_e, of both EDCs, at $C_e = 3\times10^{-5}$ mol/L, the equilibrium amount adsorbed, X_e, of BPA corresponded to ca. 7×10^{-4} mol/g, on the other hand, that of DEP corresponded to ca. 5.5×10^{-4} mol/g. In a higher equilibrium concentration region, at $C_e = 1.2\times10^{-4}$ mol/L, the X_e of BPA corresponded to ca. 1.1×10^{-3} mol/g, and that of DEP corresponded to ca. 9.5×10^{-4} mol/g. In both cases, in the range of $C_e <$ ca. 1.0×10^{-4} mol/L, the abrupt increase in the adsorption amount was observed. A similar tendency has been reported in some previous studies (Oliveira et al., 2012). In addition, the adsorption isotherms obtained in this study were also comparable to the profiles of adsorption isotherms reported in some previous studies (Tsai et al., 2006; Oliveira et al., 2012). In these studies, it was reported that Freundlich isotherm was well fitted to the data than Langmuir isotherm. This fact suggested that activated carbon generally has at least two different types of adsorption sites. The Freundlich isotherm is an empirical equation and has been usually suitable for nonideal adsorption on heterogeneous surfaces, and it assumes that there are a large number and many different types of available sites acting simultaneously, each with a different free energy of sorption. We attempted to apply two site Langmuir isotherm to the data. Both isotherms were agreed well to two site Langmuir type isotherm model. The equations of the two-site Langmuir model are as follows:

$$X_{\mathrm{T}} = X_1 + X_2 \tag{1}$$

$$X_1 = \frac{K_1 X_{1\mathrm{S}} C_{\mathrm{e}}}{1 + K_1 C_{\mathrm{e}}} \tag{2}$$

$$X_2 = \frac{K_2 X_{2\mathrm{S}} C_{\mathrm{e}}}{1 + K_2 C_{\mathrm{e}}} \tag{3}$$

Where C_{e} is the equilibrium concentration of EDCs. X_{T}, X_1, and X_2 are the total amount adsorbed of EDCs, the amount absorbed at type 1 or 2 of EDCs, respectively. K_1 and K_2 are the equilibrium adsorption constant for the type 1 and type 2 sites, and $X_{1\mathrm{S}}$ and $X_{2\mathrm{S}}$ are the saturated adsorption density of type 1 and 2 sites, respectively. Langmuir's adsorption parameters could be determined by a least-squares method. The calculated lines of X_{T}, X_1, and X_2 are shown in Fig. 1. Good agreement of the experimental data and calculated line of X_{T} is recognized in Fig. 1. The adsorption onto type 1 sites greatly affected the adsorption behavior in relative a low concentration region ($C_{\mathrm{e}} < 1\times10^{-4}$ mol/L). These parameters are summarized in Table 1. Especially, the estimated values of the equilibrium adsorption constant or the saturated adsorption density of type 1 and 2 sites for both BPA and DEP were mostly the same, even though adsorbate was varied. The value of K_1 is about 130 times larger than that of K_2 for both BPA and DEP. This suggests that adsorption intensity onto the type 1 site is sufficiently stronger than that onto the type 2 site. Gonzáles-García et al. (2004) have conducted adsorption experiments of sodium dodecyl sulfate onto some activated carbon and have reported that the adsorption isotherms were reasonably well fitted by two site Langmiur equation, which shows a sharp increase in adsorption amount in the low equilibrium concentration region below 1×10^{-4} mol/L. The estimated values of the equilibrium adsorption constants in this study were mostly the same as the magnitude of estimated values of these by Gonzáles-García et al. (2004). In addition, Garcia et al. (2001, 2005) have also reported that non-ionic or ionic surfactants adsorption onto porous activated carbon consisted of two steps as follows: at first adsorption onto the sites of micropores (type 1 site) by more strong binding at low coverage region, second, adsorption onto the sites of mesopores (type 2 site). It could be possible to be considered that these two adsorption steps might be influenced by the present adsorption system.

We compared the estimated Langmuir adsorption isotherm parameters, that is, the equilibrium adsorption constant and the saturated adsorption density, reported by several researchers with carbon-based adsorbent. The comparison is summarized in Table 2. K and X_s represent the equilibrium adsorption constant and the saturated adsorption density. The value of X_s reported by Arampatzidou et al. (2018) is significantly larger than that of other results. The value of K varied considerably, which may have been influenced by the pretreatment method of the used activated carbon. Due to a large number of data and slight scatter, the value of R^2 in this study is slightly lower than other results, but the saturation adsorption density is not so lower than other results. The equilibrium adsorption constants are difficult to generally compare because the present study was evaluated using two site Langmuir adsorption model.

3.2. Adsorption isotherm of BPA and DEP in a binary system

The adsorption isotherm of BAP and DEP in binary system is shown in Fig. 2. The comparison of the adsorption isotherm of the single and the binary system for BPA and DEP are also shown in Fig. 2 (Figs. 2a and 2b). In the binary system, the amount adsorbed of BPA was larger than that of DEP (Fig. 2c). In the comparison of the amount adsorbed in the single system and that in the binary system, in the case of BAP, the amount adsorbed in the single system was larger than that in the binary system in the all equilibrium concentration range. On the other hand, in the case of DEP, the amount adsorbed in the single system was especially larger than that in the binary system in the relatively high equilibrium concentration range ($C_e >$ ca. 3.0×10^{-4} mol/L). Cheeng et al. (2018) reported that in a binary system (BPA and lead ion), the amount adsorbed of BPA has not significantly changed in comparison to the single system. On the other hand, Cagnon et al. (2017) reported that in the binary system (dimethyl phthalate and diethyl phthalate), the amount of adsorbed of both phthalate has decreased in the experimental region in comparison to the single system. This tendency was similar to our result about DEP shown in Fig 3.

Based on the discussion about each single adsorption isotherm described above, the AC was suggested to have two types, weak (type 2) and strong (type 1), adsorption sites for BPA or DEP. We attempted to consider two types of adsorption mechanisms. One is competitive adsorption and the other one is non-competitive adsorption. The model formulas are as follows:

Competitive dual site Langmuir adsorption model

$$X_{\mathrm{BT}} = X_{\mathrm{BS}} + X_{\mathrm{BW}} \tag{4}$$

$$X_{\mathrm{BS}} = \frac{K_{\mathrm{BS}} N_{\mathrm{S}} C_{\mathrm{B}}}{1 + K_{\mathrm{BS}} C_{\mathrm{B}} + K_{\mathrm{DS}} C_{\mathrm{D}}} \tag{5}$$

$$X_{\mathrm{BW}} = \frac{K_{\mathrm{BW}} N_{\mathrm{W}} C_{\mathrm{B}}}{1 + K_{\mathrm{BW}} C_{\mathrm{B}} + K_{\mathrm{DW}} C_{\mathrm{D}}} \tag{6}$$

$$X_{\mathrm{DT}} = X_{\mathrm{DS}} + X_{\mathrm{DW}} \tag{7}$$

$$X_{\mathrm{DS}} = \frac{K_{\mathrm{DS}} N_{\mathrm{S}} C_{\mathrm{D}}}{1 + K_{\mathrm{DS}} C_{\mathrm{D}} + K_{\mathrm{BS}} C_{\mathrm{B}}} \tag{8}$$

$$X_{\mathrm{DW}} = \frac{K_{\mathrm{DW}} N_{\mathrm{W}} C_{\mathrm{D}}}{1 + K_{\mathrm{DW}} C_{\mathrm{D}} + K_{\mathrm{BW}} C_{\mathrm{B}}} \tag{9}$$

Non-competitive dual site Langmuir adsorption model

$$X_{\mathrm{BT}} = X_{\mathrm{BS}} + X_{\mathrm{BW}} \tag{10}$$

$$X_{\mathrm{BS}} = \frac{K_{\mathrm{BS}} N_{\mathrm{BS}} C_{\mathrm{B}}}{1 + K_{\mathrm{BS}} C_{\mathrm{B}}} \tag{11}$$

$$X_{\mathrm{BW}} = \frac{K_{\mathrm{BW}} N_{\mathrm{BW}} C_{\mathrm{B}}}{1 + K_{\mathrm{BW}} C_{\mathrm{B}}} \tag{12}$$

$$X_{\mathrm{DT}} = X_{\mathrm{DS}} + X_{\mathrm{DW}} \tag{13}$$

$$X_{\mathrm{DS}} = \frac{K_{\mathrm{DS}} N_{\mathrm{DS}} C_{\mathrm{D}}}{1 + K_{\mathrm{DS}} C_{\mathrm{D}}} \tag{14}$$

$$X_{\mathrm{DW}} = \frac{K_{\mathrm{DW}} N_{\mathrm{DW}} C_{\mathrm{D}}}{1 + K_{\mathrm{DW}} C_{\mathrm{D}}} \tag{15}$$

Where, C, K, and N represent the equilibrium adsorption concentration, the equilibrium adsorption constant, and the saturated adsorption density, respectively. The subscripts, S, W, and T represent the strong site, the weak site, and total, respectively. The subscriptions, B and D represent bisphenol-A (BPA) and diethyl phthalate (DEP).

The competitive adsorption model is based on the idea that BPA and DEP compete for each type of adsorption site. On the other hand, the non-competitive adsorption model is based on the idea that each type of adsorption site has a specific site for BPA and DEP, or BPA and DEP were adsorbed each other overlapped. The fitting of the data to each adsorption model is shown in Fig. 3. The adsorption parameters estimated by a least-squares method are summarized in Table 3. As seen in Fig. 3, judging from the superposition of the experimental data (open circle and triangle) and calculated lines (solid and dashed lines), both models agreed well to experimental data. Judging from the estimated adsorption parameters, the value of K_{DW} (4.58×10^{3} L/mol) for the competitive adsorption model is much larger than the value of K_2 (1.01×10^{4} L/mol) of DEP for the single system. The large gap between the two values does not seem to follow the results of the single system. On the other hand, judging from the comparison of the saturated adsorption capacities obtained from the model calculations, the saturated adsorption density of the single system was 1.57×10^{3} mol/g on average for BPA and DEP. The saturated adsorption densities calculated from the competitive and non-competitive adsorption models (sum of BPA and DEP) are 2.17×10^{-3} mol/g and 2.41×10^{-3} mol/g, respectively. The values obtained for the binary system are both larger than those obtained for the single system. This fact could suggest that the adsorption is no longer monolayer adsorption but partially overlapping adsorption. As seen in figure 2c, the amount adsorbed of BPA was larger than that of DEP. This might be caused by overlapping adsorption of BPA rather than DEP. Because the adsorption equilibrium constant is unlikely to vary significantly even in the binary system and the value of the coefficient of determination (R^2) for the non-competitive model, the non-competitive model is considered to be suitable in the present study.

4. Conclusion

Adsorption of bisphenol-A (BPA) and diethyl phthalate (DEP) onto activated carbon (AC) was conducted with the batch system in the single and binary systems. In the single system, two site Langmuir adsorption model was reasonably well fitted to the experimental adsorption data for BPA and DEP, suggesting the presence of strong and weak binding sites on the AC surface. Especially, the estimated equilibrium adsorption constants of two types of binding sites were mostly the same value (1.01×10^4 and 1.32×10^6 L/mol for weak and strong sites) even though different adsorbate was used. The adsorption binding intensity of the strong site inferred from the equilibrium adsorption constant is ca. 130 times larger than that of the weak site. Based on the two site Langmuir adsorption model, for the binary system, two adsorption models were attempted to explain the adsorption behavior, those are, competitive adsorption and non-competitive adsorption. The non-competitive adsorption model agreed well with the adsorption data in the binary system. Compared with the single system, in the binary system, the equilibrium adsorption constants were almost the same, but the saturated adsorption densities were 10% to 30% lower than those of the single system.

Acknowledgement

The authors are grateful to appreciate late Dr. Akira Suzuki for meaningful discussions and Mr. Hiroyuki Tamoto, former student of Department of Marine Bioresources Chemistry, Faculty of Fisheries, Hokkaido University, for his help and efforts in the experiments.

References

Abderrazik, N.B., Azmani, A., R’kiek, C., Song, W., O’Shea, K.E., 2005. Iron(II)-Catalyzed Enhancement of Ultrasonic-Induced Degradation of Diethylstilbestrol (DES). Catal. Today 101, 369-373. https://doi.org/10.1016/j.cattod.2005.03.012

Ahmadi, E., Kakavandi, B., Azari, A., Izanloo, H., Gharibi, H., Mahvi, A.H., Javid, A., Hashemi, S.Y., 2016. The performance of mesoporous magnetite zeolite nanocomposite in removing dimethyl phthalate from aquatic environments. Desalination and Water Treatment 57, 27768-27782. https://doi.org/10.1080/19443994.2016.1178174

Arampatzidou, A., Voutsa, D., Deliyanni, E., 2018. Removal of bisphenol A by Fe-impregnated activated carbons, Environmental Science and Pollution Research 25, 25869-25879. https://doi.org/10.1007/s11356-018-2652-4

Azari, A., Babaei, A.A., Rezaei-Kalantary, R., Esrafili, A., Moazzen, M., Kakavandi, B., 2014. Nitrate removal from aqueous solution using carbon nanotubes magnetized by nano zero-valent iron. Journal of Mazandaran University of Medical Sciences 23, 15-27.

Azari, A., Salari, M., Dehghani, M.H., Alimohammadi, M., Ghaffari, H., Sharafi, K., Shariatifar, N., Baziar, M., 2016. Efficiency of Magnitized Graphene Oxide Nanoparticles in Removal of 2,4-Dichlorophenol from Aqueous Solution. Journal of Mazandaran University of Medical Sciences 26, 265-281.

Baek, H.J., Park, M.H., Lee, Y.D., Kim, H.B., 2003. Effect of in vitro Xenoestrogens on Steroidogenesis in Mature Female fish, Chasmichthys dolichognathus. Fish Physiol. Biochem. 28, 413-414. https://doi.org/10.1023/B:FISH.0000030609.71170.f9

Belfroid, A., Velzen, M., Horst, B., Vethaak, D., 2002. Occurrence of Bisphenol A in Surface Water and Uptake in Fish: Evaluation of Field Measurements. Chemosphere 49, 97-103. https://doi.org/10.1016/S0045-6535(02)00157-1

Cagnon, B., Chatelain, S., Oliveira, T.F., Versaveau, F., Delpeux, S., Chedeville, O., 2017. Adsorption of phthalates on activated carbons in monosolute solution and in mix within complex matrices, Water Air Soil Pollut., 228, 144. https://doi.org/10.1007/s11270-017-3315-7

Chang, K.L., Hsieh, J.F., Ou, B.M., Chang, M.H., Hseih, W.Y., Lin, J.H., Huang, P.J., Wong, K.F., Chen, S.t., 2012. Adsorption studies on the removal of an endocrine-disrupting compound (bisphenol A) using activated carbon from rice straw agricultural waste, Separation Science and Technology 47, 1514-1521. https://doi.org/10.1080/01496395.2011.647212

Choong, C.E., Ibrahim, S., Yoon, Y., Jang, M., 2018. Removal of lead and bisphenol A using magnesium silicate impregnated palm-shell waste powdered activated carbon: comparative studies on single and binary pollutant adsorption. Ecotoxicology and Environmental Safety. 148, 142-151. http://dx.doi.org/10.1016/j.ecoenv.2017.10.025

Coleman, H.M., Chiang, K., 2005. Amal, R. Effects of Ag and Pt on Photocatalytic Degradation of Endocrine Disrupting Chemicals in Water. Chem. Eng. J. 113, 65-72. https://doi.org/10.1016/j.cej.2005.07.014

Den, W., Liu H.C., Chan, S.F., Kin, K.T, Huang, C., 2006. Adsorption of phthalate esters with multiwalled carbon nanotubes and its applications, Journal of Environmental Engineering and Management, 16, 275-282.

Emmerik, T., Angove, M.J., Johnson, B.B., Wells, J.D., Fernandes, M.B., 2003. Sorption of 17β-Estradiol onto Selected Soil Minerals. J. Colloid Interface Sci. 266, 33-39. https://doi.org/10.1016/S0021-9797(03)00597-6

González-García, C.M., Denoyel, R., González-Martín, M.L., Gómez-Serrano, V., 2001. Influence of porosity on the adsorption enthalpies of a non-ionic surfactant onto carbonaceous materials. Thermochimica Acta. 375, 177-185. https://doi.org/10.1016/S0040-6031(01)00526-3

González-García, C.M., González-Martín, M.L., Denoyel, R., Gallardo-Moreno, A.M., Labajos-Broncano, L., Bruque, J.M., 2004. Ionic surfactant adsorption onto activated carbons. J. Colloid Interface Sci. 278, 257-264. https://doi.org/10.1016/j.jcis.2004.06.012

González-García, C.M., González-Martín, M.L., Denoyel, R., Gallardo-Moreno, A.M., Labajos-Broncano, L., Bruque, J.M., 2005. Adsorption enthalpies of sodium dodecyl sulphate onto carbon blacks in the low concentration range. Carbon 43, 567-572. https://doi.org/10.1016/j.carbon.2004.10.021

Irmak, S., Erbatur, O., Akgerman, A., 2005. Degradation of 17β-Estradiol and Bisphenol A in Aqueous Medium by Using Ozone and Ozone/UV Techniques. J. Hazard. Mater. 126, 54-62. https://doi.org/10.1016/j.jhazmat.2005.05.045

Jafer, M., Ibrahim, H., Taufiq-Yap, Y.H., 2019. Bisphenol A removal from aqueous solution using waste agarwood activated carbon: kinetics and isotherm investigation of adsorption process, Eurasian Journal of Analytical Chemistry 14, 32-41. Eurasian J Anal Chem 14, 32-41.

Kashiwada, S., Ishikawa, H., Miyamoto, N., Ohnishi, Y., Magara, Y., 2002. Fish Test for Endocrine-Disruption and Estimation of Water Quality of Japanese Rivers. Water Res. 36, 2161-2166. https://doi.org/10.1016/S0043-1354(01)00406-7

Kubo, T., Hosoya, K., Sano, T., Nomachi, M., Tanaka, N., Kaya, K., 2005. Selective Separation of Brominated Bisphenol A Homologues Using a Polymer-Based Medium Prepared by the Fragment Imprinting Technique. Anal. Chim. Acta 549, 45-50. https://doi.org/10.1016/j.aca.2005.06.015

Kumar, A.J., Namasivayam C., 2014. Uptake of endocrine disruptor bisphenol-A onto sulphuric acid activated carbon developed from biomass: equilibrium and kinetic studies. Sustain. Environ. Res. 24, 73-80.

Lahnsteiner, F., Berger, B., Kletzl, M., Weismann, T., 2005. Effect of Bisphenol A on Maturation and Quality of Semen and Eggs in the Brown Trout. Aquat. Toxicol. 75, 213-224. https://doi.org/10.1016/j.aquatox.2005.08.004

Libbrecht, W., Vandaele, K., Buysser, K.D., Verberckmoes, A., Thybaut, J.W., Poelman, H., Clercq, J.D., Van der Voort, P., 2015. Tuming the pore geometry of ordered mesoporous carbons for enhanced adsorption of bisphenol-A, Materials 8, 1652-1665. https://doi.org/10.3390/ma8041652

Martín-Lara, M.A., Calero, M., Ronda, A., Iáñez-Rodríguez, I., Escudero, C., 2020. Adsorptive behavior of an activated carbon for bisphenol A removal in single and binary (bisphenol A—heavy metal) solutions. Water, 12, 2150-2169. https://doi.org/10.3390/w12082150

Modaressi, K., Taylor, K.E., Bewtra, J.K., Biswas, N., 2005. Laccase-Catalyzed Removal of Bisphenol-A from Water: Protective Effect of PEG on Enzyme Activity. Water Res. 39, 4309-4316. https://doi.org/10.1016/j.watres.2005.08.005

Mohan, S.V., Shailaja, S., Krishna, M.R., Sarma, P.N., 2007. Adsorptive removal of phthalate ester (diethyl phthalate) from aqueous phase by activated carbon: a kinetic study. J. Hazardous Materials. 146, 278-282. https://doi.org/10.1016/j.jhazmat.2006.12.020

Nagae, M., Shiroyama, K., Inoue, M., Hara, A., Takao, Y., Kohra, S., Ishibashi, Y., Tominaga, N., Yoshihara, S., Arizono, K., 2005, Estrogenic Potency of a Bisphenol A Metabolite on Vitellogenin Synthesis in Medaka, Oryzias latipes. J. Health Sci. 51, 93-95. https://doi.org/10.1248/jhs.51.93

Naghan, D. J., Azari, A., Mirzaei, N., Velayati, A., Tapouk, F.A., Adabi, S., Pirsaheb, M., Sharafi, K., 2015. Parameters effecting on photocatalytic degradation of the phenol from aqueous solutions in the presence of ZnO nanocatalyst under irradiation of UV-C light. Bulgarian Chemical Communications 47, 14-18.

Naganathan, K.K., Mohd Faizal, A.N., Ahmad Zaini, M.A., Ali, A., 2021. Adsorptive removal of bisphenol A from aqueous solution using activated carbon from coffee residue, Materials Today: Proceedings. https://doi.org/10.1016/j.matpr.2021.02.802

Nakada, N., Nyunoya, H., Nakamura, M., Hara, A., Iguchi, T., Takada, H., 2004. Identification of Estrogenic Compounds in Wastewater Effluent. EnViron. Toxicol. Chem. 23, 2807-2815. https://doi.org/10.1897/03-699.1

Nakanishi, A., Tamai, M., Kawasaki, N., Nakamura, T., Tanada, S., 2002. Adsorption Characteristics of Bisphenol A onto Carbonaceous Materials Produced from Wood

Chips as Organic Waste. J. Colloid Interface Sci. 252, 393-396. https://doi.org/10.1006/jcis.2002.8387

Ohkubo, N., Mochida, K., Adachi, S., Hara, A., Hotta, K., Nakamura, Y., Matsubara T., 2003. Estrogenic Activity in Coastal Areas around Japan Evaluated by Measuring Male Serum Vitellogenins in Japanese Common Boby Acanthogobius flaVimanus. Fish. Sci. (Carlton, Aust.) 69, 1135.

Oliveira, T.F., Cagnon, B., Fauduet, H., Licheron, M., Chedeville, O., 2012. Removal of diethyl phthalate from aqueous media by adsorption on different activated carbons: kinetic and isotherm studies. Separation Science and Technology, 47 1139-1148. https://doi.org/10.1080/01496395.2011.645184

Rahmani, J., Miri, A., Mohseni-Bandpei, A., Fakhri, Y., Bjørklund, G., Keramati, H., Moradi, B., Amanidaz, N., Shariatifar, N., Khaneghah, A.M., 2019. Contamination and prevalence of histamine in canned tuna from Iran: A systematic review, meta-analysis, and health risk assessment. Journal of Food Protection 81(12), 2019-2027. https://doi.org/10.4315/0362-028X.JFP-18-301

Shareef, A., Angove, M.J., Wells, J.D., Johnson, B.B., 2006. Sorption of Bisphenol A, 17R-Ethynylestradiol and Estrone to Mineral Surfaces. J. Colloid Interface Sci. 297, 62-69. https://doi.org/10.1016/j.jcis.2005.10.039

Sohoni, P., Tyler, C.R., Hurd, K., Caunter, J., Hetheridge, M., Williams, T., Woods, C., Evans, M., Toy, R., Gargas, M., Sumpter, J.P., 2001. Reproductive Effects of Long-Term Exposure to Bisphenol A in the Fathead Minnow (Pimephales promelas). Environ. Sci. Technol. 35, 2917-2925. https://doi.org/10.1021/es000198n

Sudhakar, P., Mall, I.D., Srivastava, V.C., 2016. Adsorptive removal of bisphenol-A by rice husk ash and granular activated carbon - a comparative study. Desalination and Water Treatment, 57, 12375-12384. https://doi.org/10.1080/19443994.2015.1050700

Sumpter, J.P., Johnson, A.C., 2005. Lessons from Endocrine Disruptor and Their Application to Other Issues Concerning Trace Organics in the Aquatic Environment. Environ. Sci. Technol. 39, 4321-4332. https://doi.org/10.1021/es048504a

Toledo, I.B., Ferro-García, M.A., Rivera-Utrilla, J., Moreno-Castilla, C., Vegas Fernández, F.J., 2005. Bisphenol A removal from water by activated carbon. effects of carbon characteristics and solution chemistry. Environ. Sci. Technol. 39, 6264-6250. https://doi.org/10.1021/es0481169

Tsai, W.T., Lai, C.W., Su, T.Y., 2006. Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorbents. J. Hazardous Materials. B134, 169-175. https://doi.org/10.1016/j.jhazmat.2005.10.055

Tsue, H., Takimoto, T., Kikuchi, C., Yanase, H., Takahashi, H., Amezawa, K., Ishibashi, K., Tanaka, S., Tamura, R., 2005. Adsorptive Removal of Bisphenol A by Calix[4]crown Derivatives: Significant Contribution of Hydrogen Bonding Interaction to the Control of Adsorption Behavior. Chem. Lett. 34, 1030-1031. https://doi.org/10.1246/cl.2005.1030

Zhao, Y., Cho, C.W., Cui, L., Wei, W., Cai, J., Wu, G., Yun, Y.S., 2019. Adsorptive removal of endocrine-disrupting compounds and pharmaceutical using activated charcoal from aqueous solution: kinetics, equilibrium, and mechanism studies, Environmental Science and Pollution Research 26, 33897-33905.

https://doi.org/10.1007/s11356-018-2617-7

List of figure captions and table titles

Fig. 1. Adsorption isotherm of (a) bisphenol-A (BPA) and (b) diethyl phthalate (DEP). The solid lines in figures are the calculation line based on two site Langmuir adsorption model. The dashed and dotted lines in figures are calculation lines of strong and weak adsorption of two site Langmuir adsorption model, respectively.

Fig. 2. Comparison of the adsorption isotherm in single and binary system for (a) bisphenol-A (BPA) and (b) diethyl phthalate (DEP), respectively. The adsorption isotherm in binary system (c) for BPA (open circle) and DEP (open triangle), respectively.

Fig. 3. Fitting of the data to (a) the competitive adsorption model (Eqs. (4)-(9)) and (b) non-competitive adsorption model (Eqs. (10)-(15)), respectively. The open circle and triangle correspond to bisphenol-A (BPA) and diethyl phthalate (DEP), respectively.

Table 1 The estimated parameters of the dual site Langmiur adsorption model for BPA and DEP.

Table 2 Comparison of estimated Langmuir adsorption isotherm parameters for BPA and DEP.

Table 3 The estimated parameters of competitive adsorption model and non-competitive adsorption model.

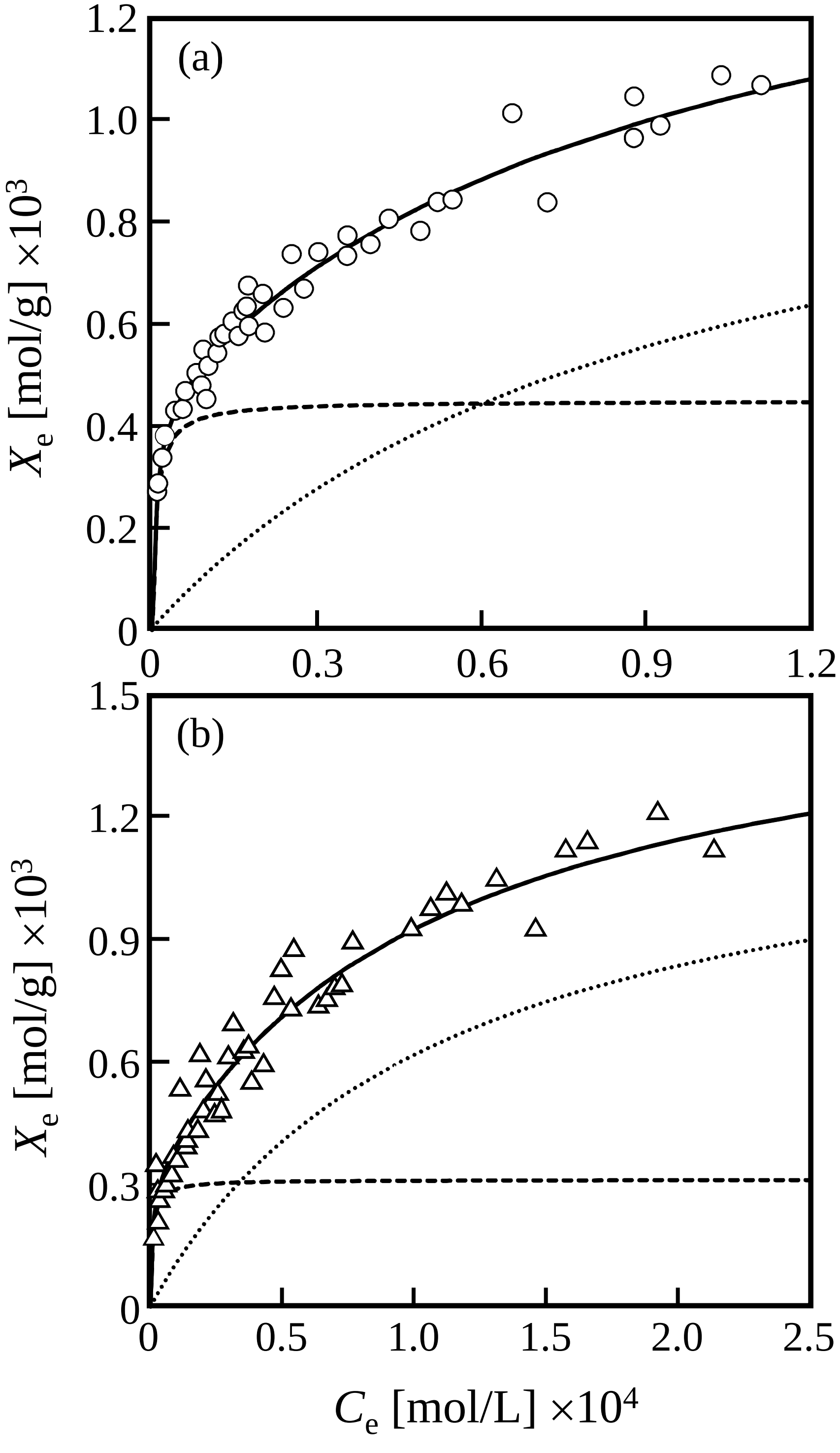

Fig. 1. Adsorption isotherm of (a) bisphenol-A (BPA) and (b) diethyl phthalate (DEP). The solid lines in figures are the calculated line based on two site Langmuir adsorption model. The dashed and dotted lines in figures are calculated lines of strong and weak adsorption of two site Langmuir adsorption model, respectively.

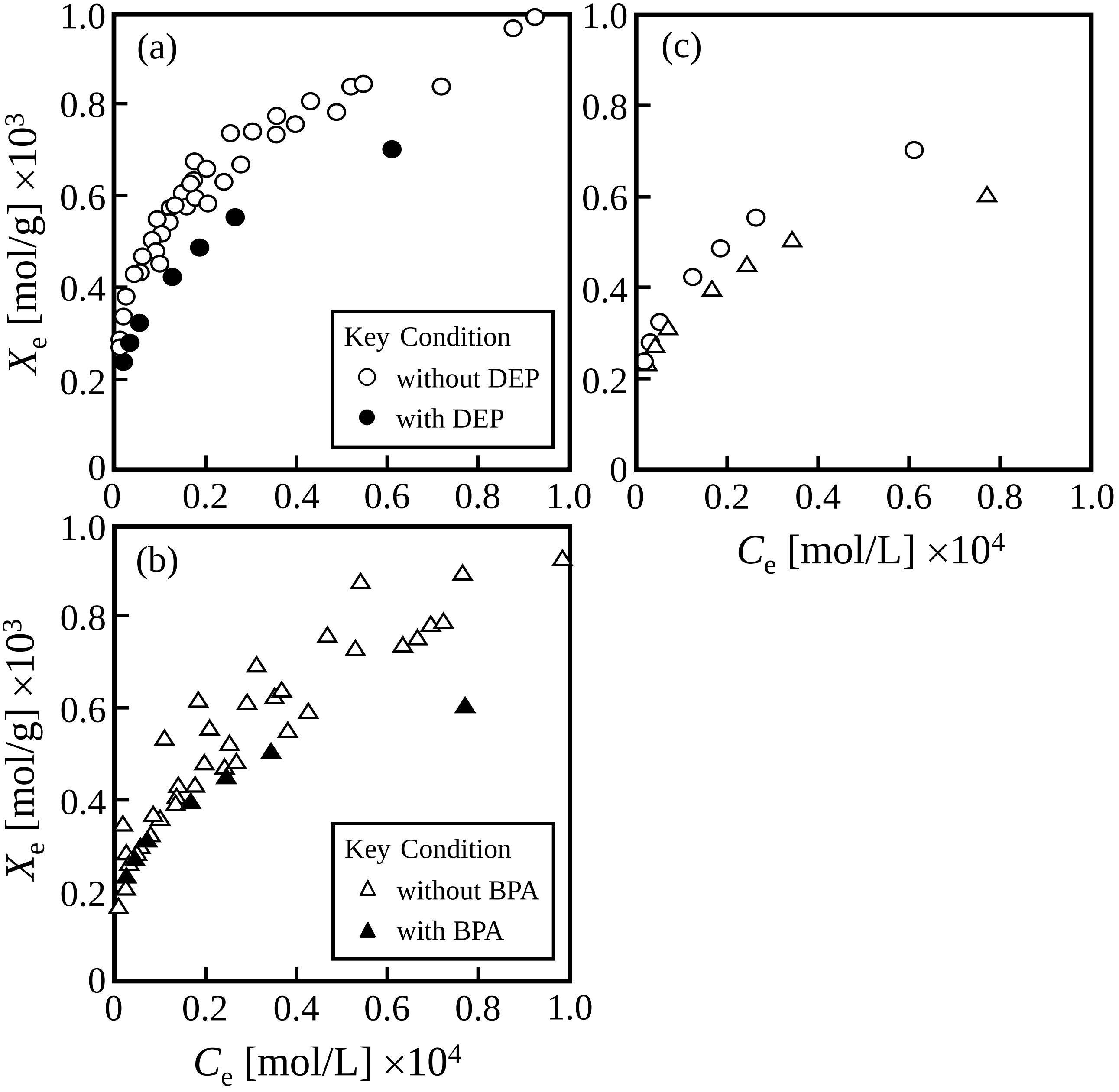

Fig. 2. Comparison of the adsorption isotherm in single and binary system for (a) bisphenol-A (BPA) and (b) diethyl phthalate (DEP), respectively. The adsorption isotherm in binary system (c) for BPA (open circle) and DEP (open triangle), respectively.

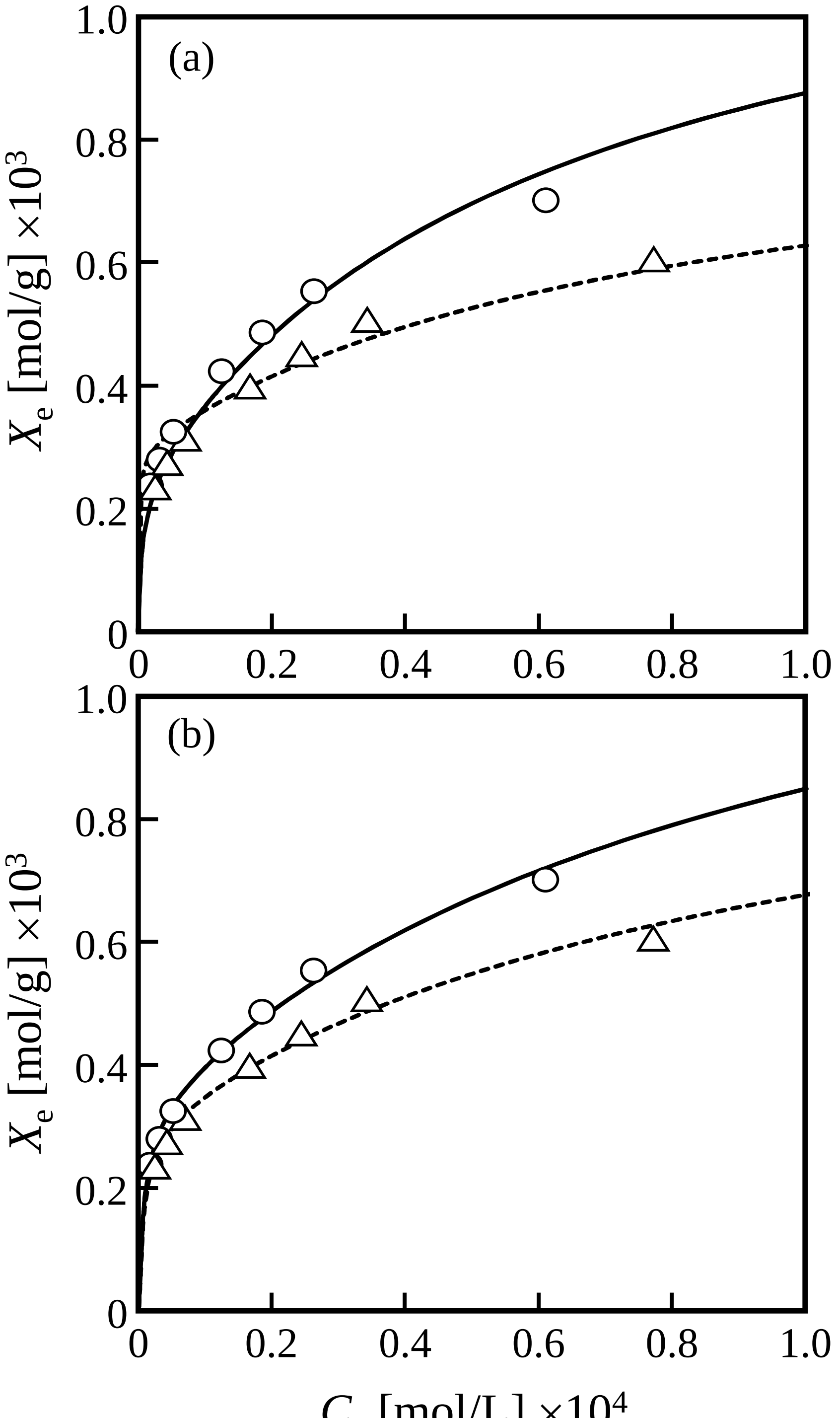

Fig. 3. Fitting of the data to (a) the competitive adsorption model (Eqs. (4)-(9)) and (b) non-competitive adsorption model (Eqs. (10)-(15)), respectively. The open circle and triangle correspond to bisphenol-A (BPA) and diethyl phthalate (DEP), respectively.

Table 1 The estimated parameters of the dual site Langmiur adsorption model for BPA and DEP.

		Type 1	Type 2
BPA	K [L/mol]	1.32×10^{6}	1.02×10^{4}
	X_S [mmol/g]	4.50×10^{-4}	1.15×10^{-3}
DEP	K [L/mol]	1.32×10^{6}	1.01×10^{4}
	X_S [mmol/g]	3.35×10^{-4}	1.21×10^{-3}

Table 2 Comparison of estimated Langmuir adsorption isotherm parameters for BPA and DEP.

BPA

Adsorbent	K [L/mg]	X_S [mg/g]	R^2 [-]	Reference
AC (rice straw waste)	0.725	181.82	0.99	Chang et al., 2012
porous AC	0.64	307	0.98	Libberecht et al., 2015
wood-based AC impregnated with Fe	0.11	785.65	0.97	Arampatzidou et al., 2018
waste agarwood AC	1.041	439	0.99	Jafer et al., 2019
activated charcoal	0.163	255	0.98	Zhao et al., 2019
commercial AC	0.64	91.9	0.99	Martin-Lala et al., 2020
AC (coffee residue)	0.504	155	0.98	Naganathan et al., 2021
commercial AC	0.0446[a]	263.6[a]	0.97	This study
	5.77[b]	102.6[b]		

DEP

Adsorbent	K [L/mg]	X_S [mg/g]	R^2 [-]	Reference
carbon nanotube	1.21	0.0148	0.80	Den et al., 2006
acidic treated AC	0.197	373.3	0.98	Cagnon et al., 2017
basic treated AC	0.692	257.7	0.97	
activated charcoal	0.136	293.4	0.98	Zhao et al., 2019
commercial AC	0.041[a]	286[a]	0.91	This study
	5.79[b]	68.8[b]		

a : weak site
b : strong site

Table 3 The estimated parameters of competitive adsorption model and non-competitive adsorption model.

Competitive	Strong (type 1)	Weak (type 2)	coefficien of determination
BPA	K_{BS} [L/mol]	K_{BW} [L/mol]	R^2
	1.32×10^6	1.02×10^4	0.9753
DEP	K_{DS} [L/mol]	K_{DW} [L/mol]	R^2
	1.32×10^6	4.58×10^3	0.9214
	N_{S} [mmol/g]	N_{W} [mmol/g]	
	5.33×10^{-4}	1.64×10^{-3}	
Non-competitive	Strong (type 1)	Weak (type 2)	coefficien of determination
BPA	K_{BS} [L/mol]	K_{BW} [L/mol]	R^2
	1.32×10^6	1.02×10^4	0.9921
	X_{BS} [mmol/g]	X_{BW} [mmol/g]	
	3.16×10^{-4}	1.05×10^{-3}	
DEP	K_{DS} [L/mol]	K_{DW} [L/mol]	R^2
	1.32×10^6	1.02×10^4	0.9861
	X_{DS} [mmol/g]	X_{DW} [mmol/g]	
	2.94×10^{-4}	7.59×10^{-4}	