Check for updates

Adsorption Science & Technology

Research Article

Adsorption Science & Technology
2017, Vol. 35(3–4) 339–356
© The Author(s) 2016
Reprints and permissions:
sagepub.co.uk/journalsPermissions.nav
DOI: 10.1177/0263617416676819
journals.sagepub.com/home/adt
SAGE

Adsorption of Bisphenol-A by *Eucalyptus* bark/magnetite composite: Modeling the effect of some independent parameters by multiple linear regression

Behzat Balci and Fatma Elcin Erkurt
Department of Environmental Engineering, Cukurova University, Turkey

Abstract

In the present study, *Eucalyptus camaldulensis* bark/magnetite composite was used for potential application as a low-cost adsorbent for the removal Bisphenol-A. The effects of various independent parameters, contact time, initial Bisphenol-A concentration, temperature, pH, and *Eucalyptus camaldulensis* bark/magnetite composite dosage on adsorption were investigated. It was found that the adsorption capacity of *Eucalyptus camaldulensis* bark/magnetite composite increases with the increasing of Bisphenol-A concentration, temperature, and decreasing dosage of *Eucalyptus camaldulensis* bark/magnetite composite. The adsorption capacity was found to be 290.6 mg/g with 0.1 g *Eucalyptus camaldulensis* bark/magnetite composite at pH 7 and 50°C. The Freundlich isotherm model described the adsorption process better ($R^2 = 0.998$) than the Langmuir, Dubinin–Radushkevich, Jovanovic, and Vieth–Sladek isotherm models. According to multiple linear regression analysis, *Eucalyptus camaldulensis* bark/magnetite composite dosage is the most effective parameter on adsorption capacity at equilibrium and independent variables accounted for 79.4% of the total variability of equilibrium adsorption capacity of *Eucalyptus camaldulensis* bark/magnetite composite.

Keywords

Eucalyptus camaldulensis, magnetite, Bisphenol-A, adsorption, multiple linear regression

Submission date: 11 March 2016; Acceptance date: 5 October 2016

Introduction

Bisphenol-A (BPA) is widely used in producing various organic chemical substances, epoxy resins, and polycarbonate plastics. Many studies have concluded that BPA is an endocrine

Corresponding author:
Behzat Balci, Department of Environmental Engineering, Cukurova University, Balcali, Saricam, Adana 01136, Turkey.
Email: behzatbalci@gmail.com

disrupting chemical, and it is classified as a chemical that should be removed (Auriol et al., 2006; Chapin et al., 2008; Esplugas et al., 2007; Lister and Van Der Kraak, 2001; Roy et al., 2009). Studies have shown that BPA is associated with certain diseases such as cancer, diabetes, liver, kidney, and brain function disorders, sperm count reduction, early sexual maturation in females, obesity prevalence, and immunodeficiency (Chung et al., 2011; Gong et al., 2010; Kundakovich et al., 2013; Wetherill et al., 2002). Additionally, some researchers have reported that the effective removal of BPA is vital to maintaining public human health (Joseph et al., 2011).

BPA has been found in water, surface waters, ground waters, wastewaters, sediments, sewage sludges, landfill leachates, influents and effluents of wastewater treatment plants, garbage leakages, and even tap water (Bruchet et al., 2014; Focazio et al., 2008; Furhacker et al., 2004; Jardim et al., 2012; Nie et al., 2012; Seyhi et al., 2011, 2013; Shao et al., 2008; Urbatzka et al., 2007; Vethaak et al., 2005; Yamamoto et al., 2001), revealing the potential risk of public exposure to BPA. For example, the maximum concentrations of BPA were found to be 17.2 mg/L in waste landfill leachates (Yamamoto et al., 2001).

Adsorption is a widely used and effective physical method for the treatment of colored wastewater. Adsorption systems have gained prominence as treatment processes that ensure good quality effluents that are low in concentrations of dissolved organic compounds (Walker and Weatherley, 1997). It is important to develop technologies available for water treatment. Generally, these technologies should be cost-effective, highly efficient, and easy to handle (Khalid et al., 2015). The magnetic particle technology has received considerable attention in recent years to solve environmental problems (Luiz et al., 2004). The magnetite (Fe_3O_4) nanoparticles can be used as a surface coating material in adsorption processes for enhancing the surface properties of adsorbents. These nano-adsorbents have attracted substantial interest in adsorption studies because of their high surface area and highly active surface sites (Nethaji et al., 2013). Nano adsorbents can be easily collected from liquid phase by magnetic field (Khalid and Asem, 2014).

The main objective of this study is to investigate the potential use of *Eucalyptus camaldulensis* bark/magnetite composite (EBMC) as a novel low-cost adsorbent for removal of BPA and to evaluate efficiency of multiple linear regression (MLR) for modeling adsorption behavior.

The *Eucalyptus camalduensis* barks were selected as a low-cost adsorbent because of their renewable character, wide availability, and easy collection.

Material and methods

Preparation of the EMBC

In the south region of Turkey, *E. camaldulensis* is a common species. It is native to Australia. Large evergreen tree *E. camaldulensis* has 24–40 m high and its stout trunk is often short and crooked, to 2 m in diameter and crown open, widely spreading irregular. Their barks are smooth, white, gray, or buff (Little, 1983). Since the *E. camaldulensis* barks are free of cost from any processing industries, only the transport cost is involved for the tertiary wastewater treatment. The barks of *E. camaldulensis* were collected from Balcali campus of the University of Cukurova (Adana, Turkey). Upon collection, barks were crushed and sieved to 0.125 mm particle size and washed with distilled water to remove impurities.

The EBMC was prepared by co-precipitation technique. A suspension of 5 g of EBMC in a 2000 mL of solution containing 5.82 g $FeCl_3{\cdot}6H_2O$ and 3 g $FeSO_4.7H_2O$ stirred at 70°C

for 1.5 h under N_2 atmosphere. Then a NaOH solution (5 mol/L) was added dropwise to the precipitate iron oxide. The mixtures were aged at 70°C for 3 h, then washed with distilled water and dried at 60°C for 24 h.

BPA

Preparation of a stock solution of BPA was achieved using distilled water. The structure of BPA is shown in Figure 1. Physical properties and toxicity of BPA are shown in Table 1. In all, 1000 mg/L stock solution of BPA was prepared in 5% methyl alcohol and 95% distilled water mixture. BPA solutions with desired concentrations were prepared by dilutions using distilled water.

Analyses of BPA

The BPA concentrations in solutions were determined by a high pressure liquid chromatography (HPLC) vessel (Perkin Elmer). Extraction of BPA was performed by OASIS HLB cartridges, first cartridge was conditioned with 3 mL of methanol and 3 mL of water. Then 3 mL sample was loaded to the OASIS HLB cartridge with 1 mL/min flow rate. The cartridge was washed with 3 mL of 5% methanol for removal of weak polar impurities. At the last stage, BPA was eluted by methanol with desired volume. Determination of the BPA concentrations was achieved using HPLC/UV detection device

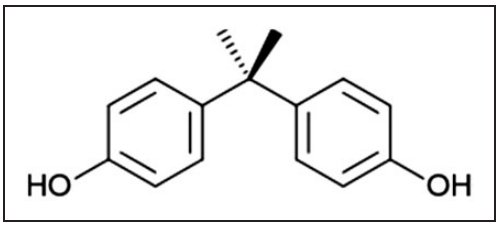


Figure 1. Chemical structure of BPA.

Table 1. Properties and toxicity of the BPA (Chen et al., 2002; Ocampo-Pérez et al., 2012; Staples et al., 1998).

Property	Value
Molecular weight (g/mol)	228.29
Molecular size (x,y,z)	$1.27 \times 0.86 \times 0.68$
V_A[a] (cm^3/mol)	294
Solubility in water (g/L)	0.09
Specific gravity (g/cm^3)	1.09–1.19
pK_a	9.6
Log K_{ow}	3.4
48-h EC_{50} (*D. manga*) (mg/L)	10

[a]Liquid molar volume at the normal boiling point.

at 278 nm. Hundred percent methanol was used as mobile phase. Zorbax Eclipse XDB-C18 column (4.6×150 mm^2) 5 μm was used. Injection volume and flow rate were 10 μL and 1.0 mL/min, respectively (Chen et al., 2008).

Statistical methods

MLR analysis is generally used in environmental studies to determine the cumulative effects of several independent variables on the dependent variable.

Mathematical expression of MLR can be represented as:

$$Y = a_0 + a_i X_i + a_2 X_2 \cdots + a_n X_n + \varepsilon \tag{1}$$

where Y is the dependent (predicted) variable, a_i ($i = 0,\ldots,n$) are the regression coefficients, X_i ($i = 1,\ldots,n$) are the independent variables (predictors) and ε shows stochastic error of the regression (Utkan et al., 2011). In this study, MLR analysis was performed to examine the cumulative effects of independent variables such as contact time, pH, temperature, BPA concentration, and adsorbent dosage on the equilibrium adsorption capacity of EBMC as a depended variable. SPSS statistics 20.0 was used for MLR analyses.

Adsorption experiments

The batch experiments were performed for the adsorption of BPA by EBMC. In all, 500 mL erlenmeyer flasks were used, each containing 200 mL BPA solution with different concentrations and with the desired weight of EBMC. The flasks were stirred at 250 rpm in a temperature–controlled orbital shaker. The effect of contact time (ranging from 5 to 70 min), pH (ranging from 1 to 12), temperature (ranging from 5 to 55°C), initial BPA concentration (ranging from 50 to 200 mg/L), and EBMC dosage (ranging from 0.1 to 0.7 g) on adsorption were studied. The samples were withdrawn at certain time intervals during the adsorption test, centrifuged for 5 min at 4000 rpm, and supernatant was used to determine the residual BPA concentration. Controlled experiments were performed without EBMC under the same conditions of adsorption experiments. BPA removal was not detected in control experiments. All experiments were carried out triplicate and average value was used for calculations.

The amount of BPA adsorbed onto EBMC at different times was calculated from equation (2):

$$q = \frac{(C_0 - C_e)V}{W} \tag{2}$$

and BPA removal efficiency was calculated as;

$$\text{BPA removal efficiency (\%)} = \frac{C_t - C_0}{C_0} \times 100 \tag{3}$$

where q is the adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the BPA in the aqueous phase (mg/L), respectively, V is the volume of the aqueous phase (L), and W is the amount of EBMC (g).

Results and discussion

Effect of contact time

The correct representation of the dynamic adsorptive separation of the BPA from the aquatic phase onto EBMC depends on an accurate understanding of the equilibrium separation between the BPA and the EBMC (Allen et al., 2003). The equilibrium time gives the optimum time for the removal of the BPA from the aqueous solutions. The effect of contact time was performed with 0.1 g EBMC and 200 mg/L BPA at pH 7 and 20°C, the effect of contact time on the adsorption capacity of EBMC for BPA is shown in Figure 2. Forty minutes is necessary to reach equilibrium for the BPA adsorption onto the EBMC. The adsorption capacity was calculated 142.4 mg/g at equilibrium time. Forty minutes was used for equilibrium time for further experiments. However, the equilibrium time was controlled under varying parameters such as pH, temperature, the BPA concentration, and EBMC dosage.

Effect of pH

In this work, the effect of pH on the adsorption of the BPA onto the EBMC was performed while the initial BPA concentration, EBMC dosage, and temperature were fixed at 200 mg/L, 0.1 g, and 20°C, respectively. The pH value of the solution is one of the most important parameters that can alter the adsorption process. The pH value of the solution could change the charge density of the adsorbent surface, and the concentration of dissolved ions in the solution would affect the adsorption capacity of the adsorbent (Behzad et al., 2015). The effect of the pH on the adsorption of the BPA onto the EBMC is given in Figure 3. It was found that the pH has an important effect on the adsorption of BPA onto EBMC. The highest adsorption capacity of the EBMC was obtained at pH 7 (142.4 mg/g). It was determined that at acidic and basic pH values, the adsorption capacity significantly decreased (14.1 mg/L at pH 1, 31.2 mg/g at pH 12). Similar results have been reported in literature on the adsorption of BPA onto the ionic resins (Víctor-Ortega et al., 2016). At acidic and basic pH values, H^+ and OH^- may occupy the adsorption sites of EBMC. The low adsorption capacities at low and high pH values may occur due to the competitive

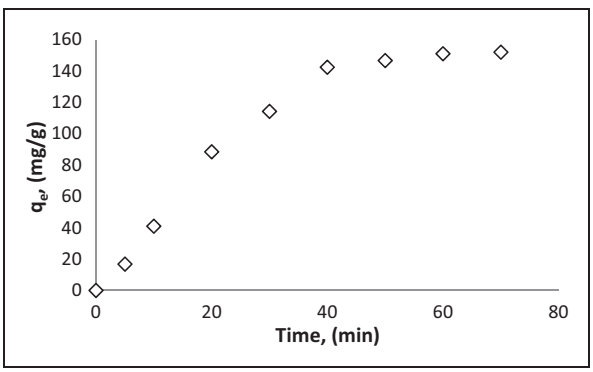


Figure 2. Equilibrium for BPA (EBMC dosage = 0.1 g, C_0 = 200 mg/L, pH = 7, T = 20°C).

adsorption between H^+, OH^- ions, and BPA molecules (Senthilkumaar et al., 2005). It was determined that 40 min is necessary to reach to equilibrium time for all pH values.

Effect of temperature

The effect of temperature (ranging from 5 to 55°C) on the adsorption of the BPA onto the EBMC was performed while the initial BPA concentration, EBMC dosage, and pH were fixed at 200 mg/L, 0.1 g, and 7, respectively (Figure 4). Temperature is an important factor that indicates whether the adsorption process is exothermic or endothermic (Ghaedi et al., 2011). The adsorption capacity of the EBMC significantly increased with the increasing temperature, which indicates that the adsorption of the BPA onto the EBMC was an endothermic process. The adsorption capacities within 40 min for 5 and 50°C were found to be 16.6 and 290.6 mg/g, respectively. The adsorption capacities for 55°C were found to be 300.6 mg/g. There were no significant differences between adsorption capacities for 50 and

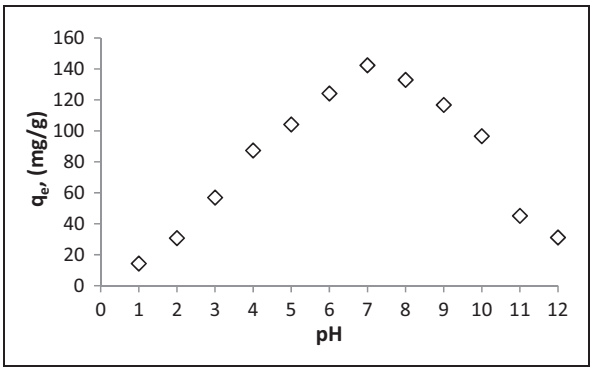


Figure 3. The effect of pH on adsorption of BPA onto EBMC (EBMC dosage = 0.1 g, C_0 = 200 mg/L, T = 20°C).

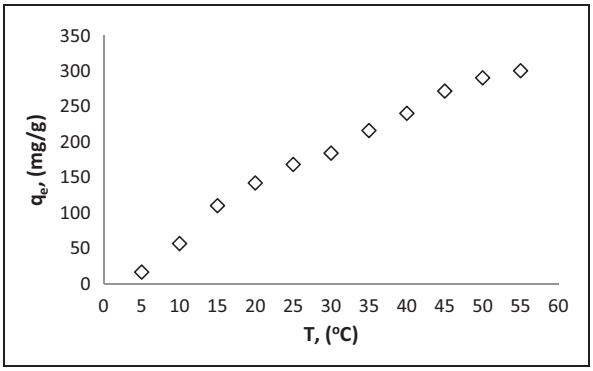


Figure 4. Effect of temperature on the adsorption of BPA onto EBMC (EBMC dosage = 0.1 g, C_0 = 200 mg/L, pH = 7).

55°C. Therefore, 50°C was selected as optimum temperature for adsorption of BPA by EBMC. Higher adsorption capacities at higher temperatures may be due to the increasing mobility of BPA molecules. Also, the number of active sites of EBMC may increase with increasing temperature (Almeida et al., 2009; Sara and Tushar, 2012; Senthilkumaar et al., 2005; Víctor-Ortega et al., 2016).

Thermodynamic parameters. The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were estimated using the following equations:

$$\Delta G^\circ = \Delta H^\circ - \mathrm{T}\Delta S^\circ \tag{4}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta H^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \tag{5}$$

where q_e is the amount of BPA adsorbed per unit mass of EBMC (mg/g) at equilibrium, C_e is equilibrium concentration (mg/L), T is temperature in K, and R is the gas constant (8.314 J/mol K) (Arias and Sen, 2009).

The thermodynamic parameters were calculated to comprehend the feasibility and nature of the adsorption of BPA onto EBMC (figure not shown). The results are presented in Table 2.

The Gibbs free energy represents the level of spontaneity of the adsorption process. High negative Gibbs free energy values indicate a more energetically favorable adsorption (Upendra, 2011). Positive ΔG° values were determined at 5 to 20°C, indicating that spontaneity is not favored at these temperatures. Generally, positive ΔG° values indicate that the adsorption reactions need some external energy source to convert reactants into products (Papita and Shamik). The negative values of ΔG° at 25 to 55°C confirmed the thermodynamic feasibility and spontaneity of the BPA adsorption onto the EBMC at these temperatures. Therefore, over 25°C solution temperature is required for the effectively removal of BPA by EBMC. The positive values of ΔH° verify the endothermic nature of BPA adsorption onto the EBMC. The adsorption capacity is increasing with the increasing

Table 2. Thermodynamic parameters of BPA adsorption onto the EBMC at different temperatures ($C_0 = 200$ mg/L, EBMC dosage = 0.1 g, pH = 7).

Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
5	3599.646	55,833.06	187.89
10	2660.196		
15	1720.746		
20	781.296		
25	−158.154		
30	−1097.6		
35	−2037.05		
40	−2976.5		
45	−3915.95		
50	−4855.4		
55	−5794.85		

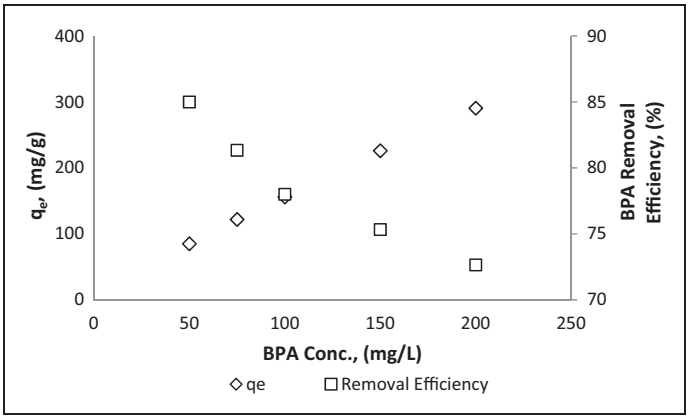


Figure 5. Effect of initial BPA concentration on the adsorption capacity of EBMC and BPA removal efficiency (EBMC dosage = 0.1 g, T = 50°C, pH = 7).

of temperature. Therefore, a temperature level over 30°C is required for the removal of BPA from aqueous solution with high removal efficiencies. The positive value of ΔS° indicates that the degree of randomness at the solid–liquid interface increased during BPA adsorption onto the EBMC (Sara and Tushar, 2012).

Effect of BPA concentration

The effect of the initial BPA concentration (ranging from 50 to 200 mg/L) on the adsorption of the BPA onto the EBMC was performed while the temperature, the EBMC dosage, and the pH were fixed at 50 mg/L, 0.1 g, and 7, respectively. It was determined that the adsorption capacity of the EBMC significantly increased with the increasing initial concentration, and the BPA removal efficiency increased with the decreasing initial BPA concentration. The effect of initial BPA concentration onto the adsorption capacity and removal efficiency is given in Figure 5. When the initial BPA concentration increased from 50 to 200 mg/L, the adsorption capacity of the EBMC increased from 85.2 to 290.6 mg/g, while the removal percentage of the BPA decreased from 85.2% to 72.6%.

Effect of the EBMC dosage

The investigation of the effects of adsorbent dosage on adsorption experiments is an important stage for determination of the adsorption capacity for the studied BPA concentrations. The effect of the EBMC dosage (ranging from 0.1 to 0.7 g) on the adsorption of the BPA onto the EBMC was performed while the initial BPA concentration, temperature, and pH were fixed at 200 mg/L, 50°C, and 7, respectively. It was found from Figure 6 that the adsorption capacity of the EBMC significantly increased from 57.08 to 290.6 mg/g with the decrease of the adsorbent dosage from 0.7 to 0.1 g. The increase in the adsorption capacity with the decreasing EBMC dosage is due to the concentration gradient between the BPA concentration in the solution and in the surface of EBMC (Sara and Tushar, 2012). It was also found that the percentage of the BPA

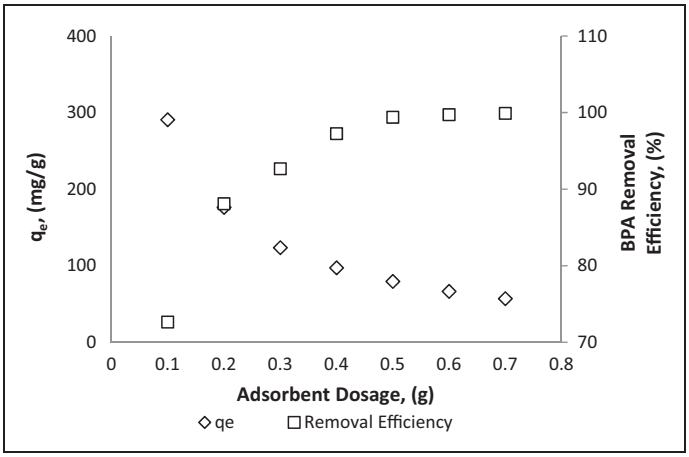


Figure 6. Effect of initial EBMC dosage on the adsorption capacity of EBMC and BPA removal efficiency ($C_0 = 200$ mg/L, $T = 50^\circ$C, pH = 7).

removal at equilibrium increased from 72.6% to 99.8% with the increase of the adsorbent mass from 0.1 to 0.7 g. This may be explained by the increase in availability of surface active sites with increasing doses of EBMC (Kannan and Sundaram, 2001). It was determined that 0.2 g EBMC was sufficient for removal of 200 mg/L BPA with a ~90% efficiency.

Equilibrium isotherms

The adsorption isotherms indicate the distribution of the adsorption molecules between the liquid phase and the solid phase at the equilibrium point. The analysis for fitting the isotherm to the adsorption isotherm models is a major stage for finding the best model to be used for the design of the adsorption systems (Kumar et al., 2010). The isotherm parameters were calculated according to the non-linear regression method due to the inherent bias resulting from the linearization of the adsorption equations. Non-linear regression ensures a mathematically sensitive method for calculating the parameters of the isotherms by using the original form of the isotherm equation (Chan et al., 2012). The minimization procedure is performed to solve the adsorption isotherm equations by maximizing the correlation coefficient between the experimental data points and the theoretical model predictions with the solver add-in function of Microsoft Excel (Wong et al., 2004). The criteria for the selection of the best isotherm model are essentially based on the correlation coefficient and the average percentage errors (APE). The correlation coefficient shows the fit between the experimental data and isotherm model, while the APE indicates the fit between the experimental data and the calculated data used for plotting the isotherm curves (Subramanyam and Ashutosh, 2012). The equation of APE can be written as:

$$APE(\%) = \frac{\sum_{i=1}^{N} \left| ((q_e)_{\exp} - (q_e)_{cal})/(q_e)_{\exp} \right|}{N} \times 100 \quad (6)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) at equilibrium, and N is the number of experimental data.

Langmuir isotherm. This model assumes monolayer adsorption on to the homogenous adsorbent surface. According to the Langmuir isotherm, the adsorbent reaches to the maximum adsorption capacity when a saturated monolayer occurred on the adsorbent surface (Khalid and Eric, 2015). When the adsorption reaches to the equilibrium, no further adsorption can occur due to the finite adsorption sites of the sorbent. The Langmuir isotherm can be represented as:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{7}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) at equilibrium, C_e is the equilibrium concentration of the adsorbate (mg/L), $q_{\max}$ is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant related to the adsorption rate (L/mg) (Langmuir, 1918).

Freundlich isotherm. Freundlich improved an empirical equation applied to define the heterogeneous adsorption processes (Freundlich, 1906). The Freundlich model can be successfully applied to the multilayer adsorption processes especially for organic molecules on the molecular sieves (Foo and Hameed, 2010). The Freundlich isotherm equation can be represented as:

$$q_e = K_F C_e^{1/n} \tag{8}$$

where K_F is the Freundlich isotherm constant (L/mg). $1/n$ represents the intensity of the surface heterogeneity and ranges between 0 and 1. A value of $1/n$ closer to zero indicates the intensity of the surface heterogeneity (Weber and Chakravorti, 1974).

Dubinin–Radushkevich (D-R) isotherm. D-R assumes the adsorbed possesses a multilayer character (Dabrowski, 2001). The model can be successfully applied to the high solute activities adsorption systems (Foo and Hameed, 2010). The equation of the D-R isotherm is given by the following equation:

$$q_e = q_{\max} \exp(-B_D \varepsilon^2) \tag{9}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

where B_D ($\mathrm{mol^2k/J^2}$) is D-R constant, ε is the Polanyi constant, R is the gas constant (8.31 J/mol K), and T is the absolute temperature (Bennani et al., 2009).

Jovanovic isotherm. The Jovanovic model was derived for an adsorption on a homogeneous solid surface, considering the phenomenon non-specific, without lateral interactions, and covering the surface with a monolayer of the solute. The equation of the Jovanovic isotherm is given as:

$$q_e = q_{\max}\left(1 - e^{(K_j C_e)}\right) \tag{11}$$

where $q_{\max}$ is the maximum adsorption capacity (mg/g) and K_j is the model constant (Rafael et al., 2013).

Vieth–Sladek isotherm. Vieth and Sladek developed a three parameters adsorption isotherm equation. The equation is a combination of a linear component and a non-linear one of the Langmuir type. The linear part corresponds to gas dissolved in the amorphous sites of a glassy polymer and the nonlinear part corresponds to gas trapped in microvoids of polymer (Crank, 1975).

$$q_e = K_{VS}C_e + \frac{q_{\max}\beta_{VS}C_e}{1 + \beta_{VS}C_e} \tag{12}$$

Estimated isotherm parameters are given in Table 3. In all, 548.48 mg/g maximum adsorption capacity of EBMC was obtained from the Langmuir isotherm with a moderate correlation coefficient (0.988) and a 2.385% APE. Also the Jovanovic isotherm predicted 365.14 mg/g adsorption capacity with a moderate correlation (0.985) and 3.194% APE. In all, 349.65 mg/g adsorption capacity of EBMC was calculated from the D-R isotherm. Among the tested isotherms, the lowest correlation coefficient (0.925) was obtained from the D-R isotherm. Therefore, an inadequate fitting of the experimental results of the adsorption isotherms is obtained using the D-R. Among the tested adsorption isotherms, which predicted the maximum adsorption capacity, best representation of the experimental results is obtained using the Vieth–Sladek model. The Vieth–Sladek isotherm predicted 343.44 maximum adsorption capacity with 0.992 correlation coefficient and 1.933% APE. Therefore, 343.44 mg/g maximum adsorption capacity was selected from the Vieth–Sladek

Table 3. Model parameters estimated for the adsorption isotherms BPA by EBMC (pH = 7, T = 50°C, EBMC dosage = 0.1 g).

Isotherms	Parameters		APE, %
Langmuir	q_{max}	548.48	2.385
	K_L	10.86	
	R^2	0.988	
Freundlich	$1/n$	0.639	0.477
	K_F	22.36	
	R^2	0.998	
D-R	q_{max}	349.65	3.503
	B_D	0.0054	
	R^2	0.925	
Jovanovic	q_{max}	365.14	3.194
	K_J	−0.0276	
	R^2	0.985	
Vieth–Sladek	q_{max}	343.44	1.933
	K_{VS}	1.331	
	β_{VS}	0.029	
	R^2	0.992	

Table 4. Adsorption capacities of various alternative adsorbents for BPA.

Adsorbent	Adsorbent capacity, mg/g	References
Bamboo	58	Goodson et al. (2004)
Almond shell	188.9	Bautista-Toled et al. (2005)
Commercial activated carbon	129.6	Bautista-Toled et al. (2005)
Hydrophobic zeolite	111.1	Wen et al. (2006)
Carbon nanotube	61	Kuo (2009)
Phenyl-functionalized mesoporous silica	351	Yong et al. (2011)
Activated rice straw	181.19	Chang et al. (2012)
Potato peel based activated carbon	133–444	Anastasia et al. (2016)
Coir pith	4.308	Zainab et al. (2015)
Coconut shell	4.159	Zainab et al. (2015)
Durian peel	4.178	Zainab et al. (2015)
Banana bunches	4.532	Zainab et al. (2015)
Coconut bunches	4.662	Zainab et al. (2015)
EBMC	*343.44*	*This study*

isotherm. According to Table 3, the coefficient of correlation of the Freundlich model is perfect (0.998) and the mean value of the APE was calculated at 0.477%. The value of 1/n (0.639) indicated favorable adsorption and intensity of the surface heterogeneity. The highest correlation coefficient and the lowest APE were obtained from the Freundlich isotherm. The Freundlich isotherm described the data very well. Therefore, the Freundlich isotherm was found to be most suitable isotherm for the adsorption of BPA onto EBMC (Bennani et al., 2009; Crank, 1975; Dabrowski, 2001; Khalid et al., 2012; Rafael et al., 2013; Weber and Chakravorti, 1974).

There are limited studies on the removal of BPA from aqueous solutions by low-cost adsorbents. Comparison of the adsorption capacities of different low-cost adsorbents for BPA under optimum experimental conditions is given in Table 4. It shows that EBMC has a large adsorption capacity compared with many other low-cost adsorbents. Adsorption capacity of activated carbon from Potato peel ranges between 133 and 444 mg/g. However, these adsorption capacities were obtained from carbonized peels under high cost methods such as different chemical and thermal conditions.

MLR analyses

MLR analysis was performed to model the effects of experimental conditions such as contact time, pH, temperature, initial BPA concentration, and EBMC dosage on the q_e values. Coefficients of MLR model are given in Table 5. The model obtained from MLR analysis is given below:

$$q_{e_{pred}} = -288.665 + 1.871X_1 + 3.681X_2 + 5.775X_3 + 1.093X_4 - 446.189X_5$$

where X_1 is the contact time, X_2 is pH value, X_3 is temperature, X_4 is BPA concentration, and X_5 is dosage of EBMC.

Table 5. Coefficients of MLR model.

	Unstandardized coefficients	Standardized coefficients			
Model	B	Std. error	Beta	t	Sig.
Constant	−288.665	33.450		−8.630	.000
Contact time	1.871	.446	.192	4.199	.000
pH	3.681	1.757	.093	2.095	.039
Temperature	5.775	.323	1.106	17.907	.000
Initial BPA conc.	1.093	.119	.491	9.183	.000
EBMC dosage	−446.189	29.915	−.833	−14.915	.000

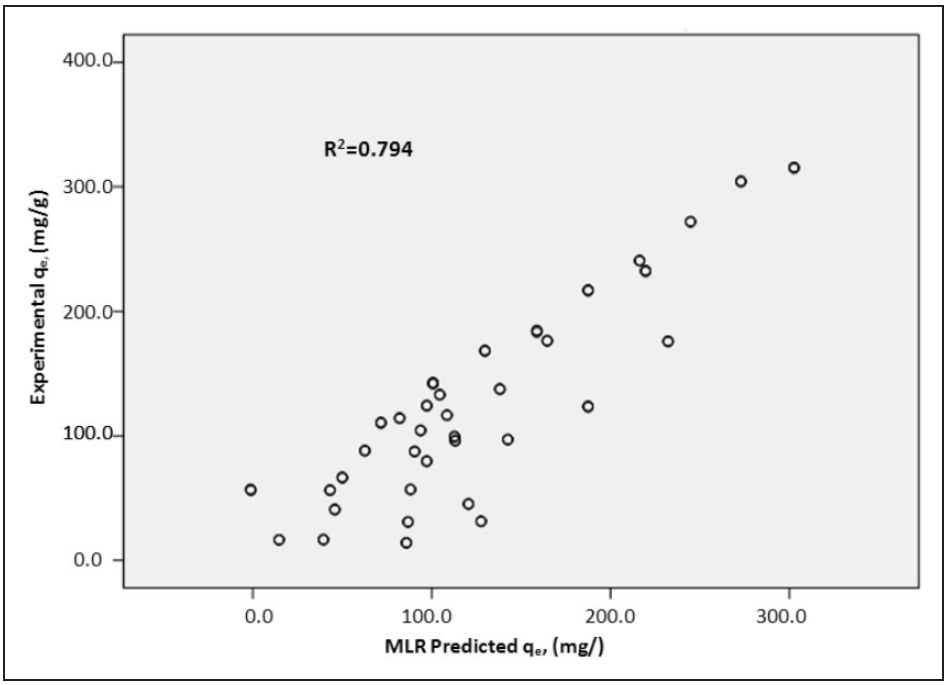


Figure 7. Experimental q_e and MLR predicted q_e.

It can be seen from Table 5. EBMC dosage is the most effective parameter on adsorption capacity at equilibrium due to the highest coefficient (−446.189). The negative value showed the negative relationship between adsorption capacity and EBMC dosage. It was mentioned above the increase in adsorption capacity with decreasing EBMC dosage is due to the concentration gradient between BPA concentration in the solution and in the surface of EBMC (Sara and Tushar, 2012). Experimental q_e and MLR predicted q_e is given in Figure 7. Correlation coefficients for experimental q_e and MLR predicted q_e were calculated as 0.794. According to the MLR, independent variables (contact time, pH, temperature, and EBMC dosage) accounted for 79.4% of the total variability of q_e.

Cost analysis of EBMC

The literature rarely reports the cost analysis of the tested adsorbents, it is important to evaluate the potential use of the adsorbents in the industrial processes. In this study, *Eucalyptus camaldulensis* barks were selected as a novel low-cost adsorbent because of their renewable character and wide availability. *Eucalyptus* is known worldwide as a source of fiber for the pulp and paper industry (Marília et al., 2014). Moreover, the abundant amounts of barks are produced during the debarking process. A simple, cost estimation was performed for the production and use of EBMC. Approximately \$200 was calculated for the production of one ton of the EMBC after considering the cost of transport, chemicals, and electrical energy. The price of the commercially activated carbon, ranges from \$700 to \$5000/ton depends on the quality (Saygili et al., 2015). Thus, the price of the EMBC is significantly cheaper than the commercially activated carbon.

Conclusion

The results of the present study show that EBMC can be used as an alternative low-cost adsorbent for the effective removal of BPA. The adsorption capacity of EBMC was found to increase with increasing initial BPA concentrations and temperature, and the adsorption capacity was found to increase with decreasing dosage of EBMC. Freundlich isotherm model could fit the experimental data perfectly ($R^2 = 0.999$). Vieth–Sladek predicted 343.44 maximum adsorption capacity with 0.992 correlation coefficient and 1.933% APE. The thermodynamic analysis showed that the adsorption of BPA onto EBMC was an endothermic process. MLR analysis showed that dosage of EBMC is the most effective parameter on adsorption capacity at equilibrium and independent variables accounted for 79.4% of the total variability of equilibrium adsorption capacity of EBMC. It was determined that only 0.2 g EBMC was sufficient for removal of 200 mg/L BPA with a ~90% efficiency from 200 mL solution. The results of this study showed that EBMC is a potential low-cost alternative adsorbent for the removal BPA by adsorption process.

Acknowledgements

The authors would like to thank Cukurova University for their support.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

References

Allen SJ, Gan Q, Matthews R, et al. (2003) Comparison of optimised isotherm models for basic dye adsorption by kuzdu. *Bioresource Technology* 88: 143–152.

Almeida CAP, Debacher NA, Downs AJ, et al. (2009) Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *Journal of Colloid and Interface Science* 332: 46–53.

Anastasia C, Arampatzidou E and Deliyanni A (2016) Comparison of activation media and pyrolysis temperature for activated carbons development by pyrolysis of potato peels for effective adsorption of endocrine disruptor bisphenol-A. *Journal of Colloid and Interface Science* 466: 101–112.

Arias F and Sen TK (2009) Removal of zinc metal ion ($Zn^{2+)}$ from its aqueous solution by kaolin clay mineral: a kinetic and equilibrium study. *Colloids and Surfaces* 348: 100–108.

Auriol M, Filali-Meknassi Y, Tyagi RD, et al. (2006) Endocrine disrupting compounds removal from wastewater a new challenge. *Process Biochemistry* 41: 525–539.

Bautista-Toled I, Ferro-García MA, Rivera-Utrilla J, et al. (2005) Bisphenol a removal from water by activated carbon, Effects of carbon characteristics and solution chemistry. *Environmental Science & Technology* 39(16): 6246–6250.

Behzad H, Susana RC, Mohammad AA, et al. (2015) Kinetics and thermodynamics of enhanced adsorption of the dye AR 18 using activated carbons prepared from walnut and poplar woods. *Journal of Molecular Liquids* 208: 99–105.

Bennani KA, Mounir B, Hachkar M, et al. (2009) Removal of basic red 46 dye from aqueous solution by adsorption onto moroccan clay. *Journal of Hazardous Materials* 168(1): 304–309.

Bruchet A, Elyasmino N, Decottignies V, et al. (2014) Leaching of bisphenol A and F from new and old epoxy coatings: Laboratory and field studies. *Water Science & Technology* 14(3): 383–389.

Chan LS, Cheung WH, Allen SJ, et al. (2012) Error analysis of adsorption isotherm models for acid dyes onto bamboo derived activated carbon. *Chinese Journal of Chemical Engineering* 20(3): 535–542.

Chang KL, Hsieh JF, Ou BM, et al. (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(10): 1514–1521.

Chapin RE, Adams J, Boekelheide K, et al. (2008) NTP-CERHR Expert Panel report on the reproductive and developmental toxicity of bisphenol A. *Birth Defects Research Part B* 83: 157–395.

Chen MY, Ike M and Fujita M (2002) Acute toxicity, mutagenicity, and estrogenicity of bisphenol-A and other bisphenols. *Environmental Toxicology* 17: 80–86.

Chen J, Huang X and Lee D (2008) Bisphenol A removal by a membrane bioreactor. *Process Biochemistry* 43: 451–456.

Chung E, Genco MC, Megrelis L, et al. (2011) Effects of bisphenol A and triclocarban on brain-specific expression of aromatase in early zebrafish embryos. *Proceedings of the National Academy of Sciences* 108(43): 17732–17737.

Crank J (1975) *The Mathematics of Diffusion* 2nd ed. London, UK: Oxford University Press.

Dabrowski A (2001) Adsorption from theory to practice. *Advances in Colloid and Interface Science* 93(1–3): 135–224.

Esplugas S, Bila DM, Kraus LGT, et al. (2007) Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials* 149: 631–642.

Focazio MJ, Kolpin DW, Barnes KK, et al. (2008) A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States II. Untreated drinking water sources. *Science of the Total Environment* 402: 2–3.

Foo KY and Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal* 156: 2–10.

Furhacker M, Scharf S and Weber H (2004) Bisphenol A: emissions from point sources. *Chemosphere* 41: 751–756.

Freundlich HM (1906) Over the adsorption in solution. *The Journal of Physical Chemistry* 57: 385–470.

Ghaedi M, Hassanzadeh A and Nasirikokhdan S (2011) Multiwalled carbon nanotubes as adsorbents for the kinetic and equilibrium study of the removal of alizarin red S and morin. *Journal of Chemical & Engineering Data* 56: 2511–2520.

Gong R, Jiang Y, Cai W, et al. (2010) Enhanced sorption of bisphenol A on ketoglutaric acid-modified chitosan resins by hydrophobic sorption of hemimicelles. *Desalination* 258: 54–58.

Goodson A, Robin H, Summerfield W, et al. (2004) Migration of bisphenol A from can coatings—effects of damage, storage conditions and heating. *Food Additives & Contaminants* 21(10): 1015–1026.

Jardim WF, Montagner CC, Pescara IC, et al. (2012) An integrated approach to evaluate emerging contaminants in drinking water. *Separation and Purification Technology* 84: 3–8.

Joseph L, Zaib Q, Khan IA, et al. (2011) Removal of bisphenol A and 17α-ethinyl estradiol from landfill leachate using single-walled carbon nanotubes. *Water Research* 45(13): 4056–4068.

Kannan N and Sundaram MM (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. *Dyes and Pigments* 51: 25–40.

Khalid ZE and Asem AA (2014) Uptake of U (VI) from aqueous media by magnetic Schiff's base chitosan composite. *Journal of Cleaner Production* 70: 292–302.

Khalid ZE and Eric G (2015) Selective removal of Hg (II) from aqueous solution by functionalized magnetic-macromolecular hybrid material. *Chemical Engineering Journal* 281: 345–359.

Khalid ZE, Hamdy AE, Abdel-Razekc AS, et al. (2012) Environmental remediation of thorium(IV) from aqueous medium onto Cellulosimicrobium cellulans isolated from radioactive wastewater. *Desalination and Water Treatment* 46: 1–9.

Khalid ZE, Gamal OE and Susan MA (2015) Removal of ferrous and manganous from water by activated carbon obtained from sugarcane bagasse. *Desalination and Water Treatment* 55: 471–483.

Kumar PS, Ramalingam S, Senthamarai C, et al. (2010) Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination* 261: 52–60.

Kundakovich M, Gudsnuk K, Franks B, et al. (2013) Sex-specific epigenetic disruption and behavioral changes following low-dose in utero bisphenol-A exposure. *Proceedings of the National Academy of Sciences* 110(24): 9956–9961.

Kuo CY (2009) Comparison with as-grown and microwave modified carbon nanotubes to removal aqueous bisphenol A. *Desalination* 249(3): 976–982.

Langmuir I (1918) Adsorption of gases on plain surfaces of glass mica platinum. *Journal of the American Chemical Society* 40: 136–403.

Lister AL and Van Der Kraak GJ (2001) Endocrine disruption: why is it so complicated? *Water Quality Research Journal of Canada* 36: 175–190.

Little EL (1983) *Common Fuelwood Crops: A Handbook for Their Identification*. West Virginia: McClain Printing Co.

Luiz CAO, Diego IP, Alessandra S, et al. (2004) Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water. *Water Research* 38: 3699–3704.

Marília P, Doahn F, Vicelina BS, et al. (2014) Evaluation on paper making potential of nine Eucalyptus species based on wood anatomical features. *Industrial Crops and Products* 54: 327–334.

Nethaji S, Sivasamy A and Mandal AB (2013) Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr (VI). *Bioresource Technology* 134: 94–100.

Nie Y, Qiang Z, Zhang H, et al. (2012) Fate and seasonal variation of endocrine-disrupting chemicals in a sewage treatment plant with A/A/O process. *Separation and Purification Technology* 84: 9–15.

Ocampo-Pérez R, Abdeldaiem MM, Rivera-Utrilla J, et al. (2012) Modeling adsorption rate of organic micropollutants present in landfill leachates onto granular activated carbon. *Journal of Colloid and Interface Science* 385(1): 174–182.

Papita S and Shamik C (2011). Insight into adsorption thermodynamics, thermodynamics. In: Tadashi M (ed). Croatia: InTech Thermodynamics.

Rafael CIF, Luis AM, Renata CFB, et al. (2013) Adsorption isotherms and thermodynamics of α-lactalbumin on an anionic exchanger. *Fluid Phase Equilibria* 348: 39–44.

Roy JR, Chakraborty S and Chakraborty TR (2009) Estrogen-like endocrine disrupting chemicals affecting puberty in humans - a review. *Medical Science Monitor* 15: 137–145.

Sara D and Tushar KS (2012) Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design. *Water Research* 46: 1933–1946.

Saygili H, Guzel F and Onal Y (2015) Conversion of grape industrial processing waste t activated carbon sorbent and its performance in cationic and anionic dyes adsorption. *Journal of Cleaner Production* 93: 84–93.

Senthilkumaar S, Varadarajan PR, Porkodi K, et al. (2005) Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies. *Journal of Colloid and Interface Science* 284: 78–82.

Seyhi B, Drogui P, Buelna G, et al. (2011) Modeling of sorption of bisphenol A in sludge obtained from a membrane bioreactor process. *Chemical Engineering Journal* 172: 61–67.

Seyhi B, Drogui P, Buelna G, et al. (2013) Biodegradation of Bisphenol-A in aerobic membrane bioreactor sludge. *Water Science & Technology* 68(9): 1926–1931.

Shao XL, Ma J and Wen G (2008) Investigation of endocrine disrupting chemicals in a drinking water work located in Songhua River Basin. *Chinese Journal of Environmental Science* 29: 2723–2728.

Staples CA, Dorn PB, Klecka GM, et al. (1998) A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere* 36: 2149–2173.

Subramanyam B and Ashutosh D (2012) Adsorption isotherm modeling of phenol onto natural soils – Applicability of various isotherm models. *International Journal of Environmental Research* 6(1): 265–276.

Upendra K (2011) Thermodynamics of the adsorption of Cd(II) from aqueous solution on NCRH. *International Journal of Environmental Science and Development* 2: 334–336.

Urbatzka R, Van Cauwenberge A, Maggioni S, et al. (2007) Androgenic and antiandrogenic activities in water and sediment samples from the river Lambro, Italy, detected by yeast androgen screen and chemical analyses. *Chemosphere* 67: 1080–1087.

Utkan O, Bilge O, Sevil V, et al. (2011) Modeling adsorption of sodium dodecyl benzene sulfonate (SDBS) onto polyaniline (PANI) by using multi linear regression and artificial neural networks. *Chemical Engineering Journal* 178(201): 183–190.

Vethaak AD, Lahr J, Schrap SM, et al. (2005) An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands. *Chemosphere* 59: 511–524.

Víctor-Ortega MD, Ochando-Pulido JM and Martínez-Ferez A (2016) Performance and modeling of continuous ion exchange processes for phenols recovery from olive mill wastewater. *Process Safety and Environmental Protection* 100: 242–251.

Walker GM and Weatherley LR (1997) Adsorption of acid dyes onto granular activated carbon in fixed beds. *Water Research* 31(8): 2093–2101.

Wong YC, Szeto YS, Cheung WH, et al. (2004) Adsorption of acid dyes on chitosan– equilibrium isotherm analyses. *Process Biochemistry* 39(6): 695–704.

Weber TW and Chakravorti RK (1974) Pore and solid diffusion models for fixed bed adsorbers. *AIChE Journal* 20(2): 228–238.

Wen TT, Hsin CH, Ting YS, et al. (2006) Adsorption characteristics of bisphenol-A in aqueous solutions onto hydrophobic zeolite. *Journal of Colloid and Interface Science* 299: 513–519.

Wetherill YB, Petra CE, Monk KR, et al. (2002) The xenoestrogen BPA induces inappropriate androgen receptor activation and mitogenesis in prostate adenocarcinoma cells. *Molecular Cancer Therapeutics* 7: 515–524.

Yamamoto T, Yasuhara A, Shiraishi H, et al. (2001) Bisphenol A in hazardous waste landfill leachates. *Chemosphere* 42(4): 415–418.

Yong HK, Byunghwan L, Kwang HC, et al. (2011) Selective adsorption of bisphenol A by organic–inorganic hybrid mesoporoussilicas. *Microporous and Mesoporous Materials* 138: 184–190.

Zainab ML, Tony H, Mohd HP, et al. (2015) Adsorption characteristics of bisphenol A onto low-cost modified phyto-waste material in aqueous solution. *Water Air Soil Pollution* 226(34): 1–11.