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RESEARCH ARTICLE

Bio-sorption of bisphenol a by the dried- and inactivated-lichen (*Pseudoevernia furfuracea*) biomass from aqueous solutions

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Abstract

Bisphenol A (BPA), which is known as one of the endocrine-disrupting chemicals (EDCs) with hydrophilic hydroxyl groups and hydrophobic aromatic groups, has been widely used in plastic industries. The chemical waste from the industry is sometimes discharges into lakes and rivers, and then these surface waters can be polluted. So, this article aims to investigate the bio-sorption process of BPA by the inactivated lichen (*Pseudoevernia furfuracea*) biomass from aqueous solution. At initial, the effect of the variables such as initial BPA concentration, solution pH, temperature, contact time and recovery rate on the bio-sorption process was investigated. From the optimal results, it has been observed that the highest removal efficiency is approximately 64% at a contact time of 3-h, the bio-sorbent concentration of 9 mg/L, initial BPA concentration of 40 mg/L, and agitation speed of 150 rpm at pH 5.0. In explaining the bio-sorption potential of lichen biomass, Langmuir and/or Redlich-Peterson isotherms with two and three parameters, respectively were observed to be better fit with the experimental isotherm data ($R^2 = 0.982$). From equilibrium data based on difference between the measured and predicted results ($q_{e,\ exp}$ and $q_{e,\ pre}$), it was shown that biosorption of BPA could be best described by the pseudo second order kinetic model with minimum sum of square error of 2.61%. In addition, it shows more film diffusion, and partly pore diffusion in linearity region in terms of kinetic sorption behaviors of BPA in the rate-limiting step as well as intra-particle diffusion according to Boyd's kinetic model with better regression coefficient than 0.981 when compared to the other used kinetic models, including Bangham's pore diffusion and Elovich kinetic models (with R^2 of 0.958 and 0.929). The thermodynamic studies showed that the biosorption process was spontaneous, and chemically feasible. Therefore, due to be low-cost, eco-friendly character, wide availability and easily accessible, the lichen biomass could be used as a promising bio-sorbent for the removal of BPA from the environment and wastewater effluents.

Keywords Lichen · *Pseudoevernia furfuracea* · Bio-sorption · Bisphenol A

Introduction

Today, the accumulation of plastic waste is becoming a serious environmental problem because of the increasing use of plastic materials in the world. The 335 million tons of plastic production was reported in 2016 all over the world [1]. About 92.4% of marine plastics are composed of micro-plastics [2], and a large amount of these materials are a presence in aquatic areas of all over the world including the water column, seas, and oceans [3]. Bisphenol A (BPA) is used for the production of some plastic polymers such as polycarbonate plastics and epoxy resins, so BPA can be considered as one of the material that adsorbed into micro-plastics (about 16.6 ng g^{-1}) in freshwater [4]. Recently, it was reported that leaching of BPA or its products from households caused human health problems [5]. For instance, bisphenol A diglycidyl ether (BADGE), which is a product of BPA, have toxic effects on human [6]. Also, Liao et al. [7] emphasized that BPA acted as an endocrine-disrupting chemical and caused a wide range of health effects in the human body. Due to these toxic effects, it is very important to eliminate BPA from the aqueous environment. Several methods such as adsorption are presented to remove BPA from the contaminated solutions [8]. Recently, the usage of biomaterials gains importance because of their eco-friendly

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and low-cost nature in the adsorption process which also defined as bio-sorption [9]. Biomaterials such as bacteria, fungi, and algae have been employed for the treatment of polluted aqueous solutions [10]. However, there is limited knowledge about the utilization of lichens in wastewater treatment. Lichens are unique models for the symbiotic relationship in nature [11]. Lichens consist of fungi and algae or cyanobacteria, and this relationship provides them some advantages such as tolerating harsh living conditions and long lifetime [12]. Also, lichens have some physical and morphological characteristics [13].

The lichen, which is called as *Pseudoevernia furfuracea,* has been utilized in medicinal and cosmetic applications since ancient times [14, 15]. The archeological remains dating to the old Egyptian period showed that *Pseudoevernia furfurace* has been utilized due to its preservative and aromatic properties [12]. However, there is limited information about the usage of lichens in wastewater treatment technologies. Recent studies reported the effective adsorbents formed from algae [10] and fungi [16] in the wastewater treatment process. It is considered that lichens, which are the symbiotic life forms of algae and fungus, can also be successful adsorbents in the wastewater treatment process. To our present knowledge, this is the first report related to BPA removal from aqueous solutions by the lichen *Pseudoevernia furfurace*a. In the current study, Lichen (*Pseudoevernia furfuracea*) biomass has been utilized as a low cost, easily accessible, eco-friendly and effective bio-sorbent for the removal of BPA from aqueous solution.

The main aim of this study is to investigate the potential of lichen as an alternative biosorbent material for the removal of BPA from aqueous solution. In that purpose, the effects of the initial concentration of BPA, biosorbent dosage, solution pH, contact time, and temperature on the biosorption efficiency were studied as they are key influencing factors. The equilibrium data, kinetic data and thermodynamic data analysis of biosorption were carried out to understand the biosorption mechanism of BPA onto the structure of Lichen biomass as a function of pH to obtain information about interaction with active surface functional groups.

Experimental

The collection and preparation of lichen biomass

The morphologically detected lichen (*Pseudoevernia furfuracea*) biomasses were collected in the central forest of Bilecik province (N 400 11.5262 ‘, E 0290 57.962’) in Turkey. The lichen samples used in this study were kept at room temperature no more than two weeks. The collected lichen samples were carried with plastic bags from the forest to the laboratory. The samples were washed with ultra-pure water, air-dried and inactivated by heating in an oven at 70 °C for 48 h in the laboratory. The dried- and inactivated-samples were cleaned carefully with plastic tweezers for removing the possible materials (soil particles, bark, and dust) under a binocular microscope (Primo Star Zeiss). The dried-lichen biomass was then grounded and sieved through the following sizes: 75–150, 150–350, 350–700, and 700–1700 μm. A fraction of 150–350 μm was used in all bio-sorption experiments.

Reagents and equipment

Ultra-pure water (resistivity of 18.2 MΩ cm) obtained by a Labconco water purification system (Kansas City, USA) was used in all experiments. All experiments were performed in triplicate. The BPA and other chemicals were supplied from Merck (Germany). The BPA concentrations remained in equilibrium were detected using a UV-Visible spectrophotometer (Shimadzu, 160 A model, Kyoto, Japan). This spectrophotometer has a wavelength accuracy of ±0.2 nm and a bandwidth of 2 nm in the wavelength range of 190–1100 nm.

Lichen biomass was characterized by FT-IR and SEM analysis. The spectral changes in the structure of lichen biomass before and after bio-sorption of BPA were monitored using a Perkin Elmer 400 FT-IR spectrophotometer. SEM images were obtained with a Leo 440 Computer Controlled Digital System.

Batch bio-sorption procedure

Bio-sorption experiments were performed by using the batch method. Stock BPA solution (100 mg L^{-1}) was prepared using deionized water. For the bio-sorption experiments, 100 mg of lichen bio-sorbent was put into 10 mL of BPA solution (100 mg L^{-1}). The bio-sorption was carried out at 25 °C and both lichen and BPA in polypropylene tubes of 10 mL were kept in a thermostatic water bath with constant agitation speed (140 rpm) for 24 h. The pH was adjusted with dilute HCl and NaOH solutions (each one, 0.2 and/or 2.0 mol L^{-1}). The concentrations of BPA in solution medium were spectrophotometrically determined by measuring the absorbance of the solutions at 287 nm with a shift of 9 nm, where BPA gives a constant absorbance at 278 nm in the range of pH 2.0–7.0, and at higher pHs than 7.0 the absorbance sharply decreases [17, 18]. % Bio-sorption rate and Q (mg g^{-1}) were calculated by using equations in Table 1.

Results and discussion

FT-IR analysis

The FT-IR analyses give important information about the functional groups having roles in the biosorption process. Before and after bio-sorption, the sample solutions in

Table 1 Isotherm, kinetic and thermodynamic equations

Model	Equation	Parameters
The adsorbed amount	$Q=\left[\frac{(C_i-C_e)V}{m}\right]$	Q_{ads}
% Bio-sorption	$\text{Bio-sorption\%}=\left[\frac{(C_i-C_f)}{C_i}\right]x100$	Bio-sorption%
% Desorption	$\text{Desorption\%}=\frac{Q_{des}}{Q_{ads}}x100$	Q_{des}
Isotherm	**Equation**	**Parameters**
Langmuir	$Q_e=\frac{X_L K_L C_e}{1+K_L C_e}$	X_L, K_L
Freundlich	$Q_e=K_F C_e^{\beta}$	K_F, β
Dubinin-Raduskevich	$Q_e=X_{DR}e^{-K_{DR}\varepsilon^2}$	X_{DR}, K_{DR}
	$\varepsilon=RTln\left(1+\frac{1}{C_e}\right)$	ε
	$E_{DR}=(2K_{DR})^{-0.5}$	E_{DR}
Redlich-Peterson	$Q_e=\frac{AC_e}{1+BC_e^g}$	A, B, g
Kinetic	**Equation**	**Parameters**
Pseudo-first-order	$Q_t=Q_e\left[1-e^{-k_1 t}\right]$	k_1, Q_e
Pseudo-second-order	$Q_t=\frac{t}{\left[\frac{1}{k_2 Q_e^2}\right]+\left[\frac{t}{Q_e}\right]}$	k_2, Q_e
Intraparticle diffusion	$Q_t=k_i t^{0.5}$	k_i
Bangham's model	$log\left(\frac{C_0}{C_0-qm}\right)=log\left(\frac{k_0 m}{2{,}303V}\right)+\alpha logt$	α, k_0
Boyd model	$F=\frac{q_t}{q_e}$	F
$Bt=-0.4977-\ln(1-F)$,	$B=\frac{\pi^2 D_i}{r^2}$	D_i
Elovich model	$Q_t=\frac{ln(\alpha\beta)}{\beta}+\frac{1}{\beta}lnt$	α, β
Thermodynamics	**Equation**	**Parameters**
The distribution coefficients	$K_D=\frac{Q}{C_e}$	K_D
The free energy of adsorption	$\Delta G^0=-RTlnK_L$	ΔG^0
Van't Hoff	$lnK_L=\frac{\Delta S^0}{R}-\frac{\Delta H^0}{RT}$	ΔH^0, ΔS^0

C_i is the initial concentration of the bio-sorbent(mg L^{-1}), C_f is the equilibrium concentration (mg L^{-1}), m refers to the bio-sorbent mass (mg) and V is the solution volume (mL), q_t: The bio-sorbed amounts at time t (mg g^{-1}), X_L: Langmuir adsorption equilibrium constant (L mg^{-1}), K_f: Freundlich constants, β; adsorbent surface heterogeneity, X_{DR}: DR constant related to the sorption energy (mol^2 K J^{-2}), ε: Polanyi potential, R: Ideal gas constant (8.314 J mol^{-1} K^{-1}), A:Redlich Peterson constant (L g^{-1}), B: Redlich Peterson constant (L $mg^{-(1-1/A)}$), g is the exponent reflecting the heterogeneity of the adsorbent, T: absolute temperature (298 K), E: Free energy change (kJ mol^{-1}), k_1(min^{-1}), k_2 (mg g min^{-1}), and k_i (mg g $min^{-0.5}$), are the rate constants, k_0 and α are Bangham's model constants, F is the fractional attainment of equilibrium, D_i is the effective diffusion coefficient, *r* is the radius of the adsorbent particle assuming spherical shape, Elovich model constants; is the initial adsorption rate (mg g^{-1} min^{-1}) and is the desorption constant (g mg^{-1}). K_D: The distribution coefficients, ΔG^0: The free energy of adsorption (kJ mol^{-1}), ΔH^0: The value of enthalpy changes (kJ mol^{-1}), ΔS^0: The value of entropy changes (kJ mol^{-1})

suspension were centrifuged at 5000 rpm for 10 min and dried in an oven at 105 °C to make sure it is in the solid phase, and their FT-IR spectra were taken. FT-IR spectra analysis results are illustrated in Fig. 1. The changes observed in the peaks at around 1300 cm^{-1} indicated the C=O stretching band of carbonyl groups [22, 23, 25, 26]. The characteristic peaks observed at around 1206–1029 cm^{-1} indicated the phosphate groups representing the P=O and P-OH stretching [24, 27]. The changes in the FT-IR spectra before and after BPA bio-sorption proved that the functional groups on the lichen biomass involved in the bio-sorption process. This also supported the chemical interactions that were formed between BPA and the surface functional groups of lichen biomass.

SEM analysis

Before and after bio-sorption, the sample solutions in suspension were centrifuged at 5000 rpm for 10 min, and dried in an oven at 105 °C to make sure it is in solid phase, and their SEM images were taken. The results were shown in Fig. 2. The SEM images showed that the particles were irregularly shaped and edged porous. The surface of the lichen biomass after bio-sorption was generally smooth and rounded, indicating that the particles deposited were BPA. This case might be because of the hydrophilic (strong hydrogen bonding) and hydrophobic (weak van der Waals and π-π stacking) interactions between BPA and the functional groups on the surface of the lichen bio-sorbent at pH 5.0.

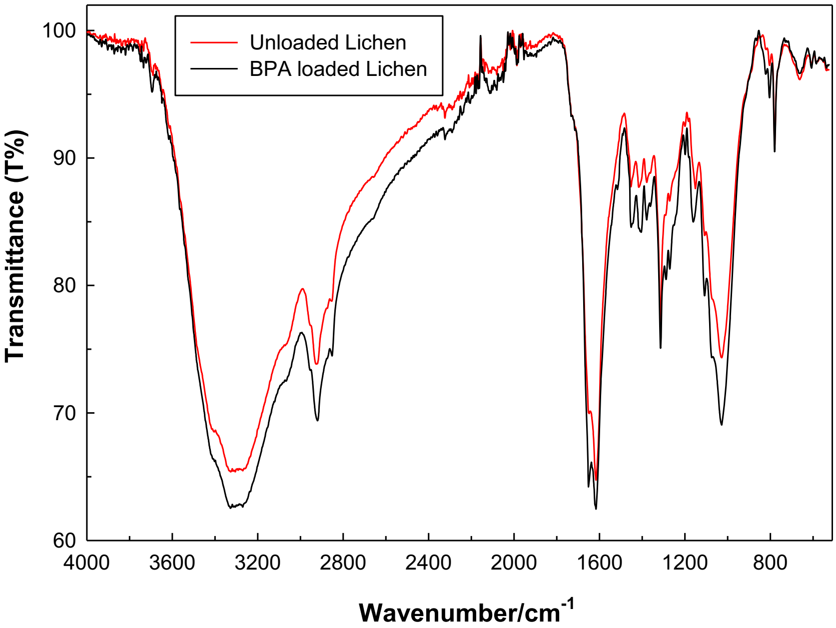


Fig. 1 FT-IR spectra of lichen bio-sorbent before and after bio-sorption of BPA

Effect of initial pH and point of zero charge, pH_{pzc} of the biosorbent

The pH of the solution is an important parameter to consider. This parameter can affect both the ionizable surface charges of the biosorbent and the protonation/deprotonation of the sorbate. The effect of pH changes depending on the type of biosorbents and the dissociation constants (pK_a) of the sorbate.

According to this pH range, the understanding of the effect of pH on biosorption characteristics is required. The influence of pH on the biosorption of BPA by the lichen biomass is shown in Fig. 3(a). In the acidic pH range, the sorption rate linearly increased from 74% to 86% in the pH range of 1.0–4.0 and reached to a maximum value or saturation point (shortly a plateau) in the pH range of 4.0–7.0, to give a stable and reproducible sorption rate at optimal pH 5.0. It may be explained by the decrease of hydronium ions after the increase of pH, which reduces the chance of competition between hydronium ions and the BPA molecules. Due to the surface functionality of the lichen biomass in the pH range of 1.0–4.0, it is possible for hydronium ions to be adsorbed by the non-ionizable proton acceptor carbonyl groups of lichen biomass through electrostatic interactions [28–30]. After a slight fluctuation in pH 7.0–9.0, the sorption rate sharply decreased at pHs above 9.0. This sharp decrease could be explained by the pK_a of BPA (9.6). In aqueous solutions, the sorbates will stay in their molecular form at pH lower than pK_a, and will lose their protons at pH above pK_a. Thus, at pH around or higher than pK_a, the BPA molecules are deprotonated to

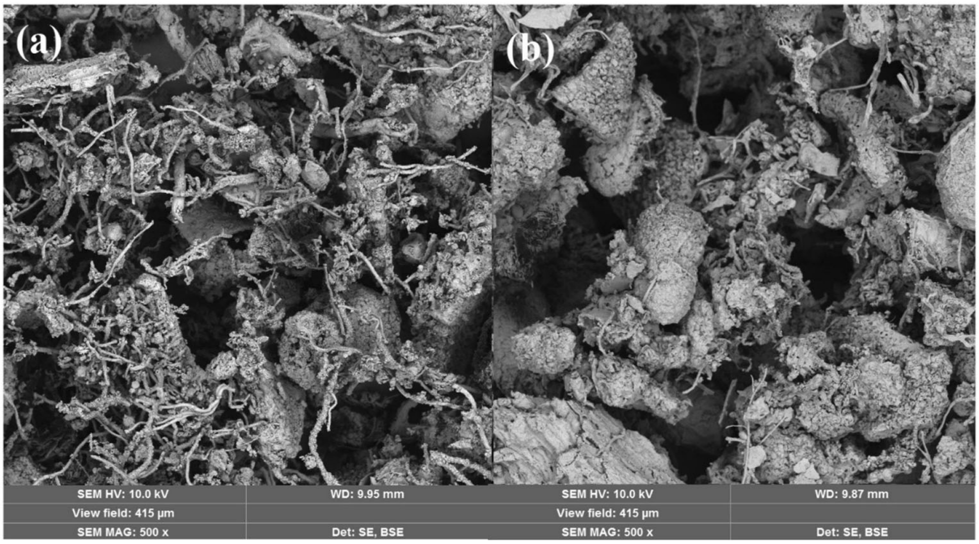


Fig. 2 SEM photographs of lichen samples before (**a**) and after (**b**) bio-sorption of BPA

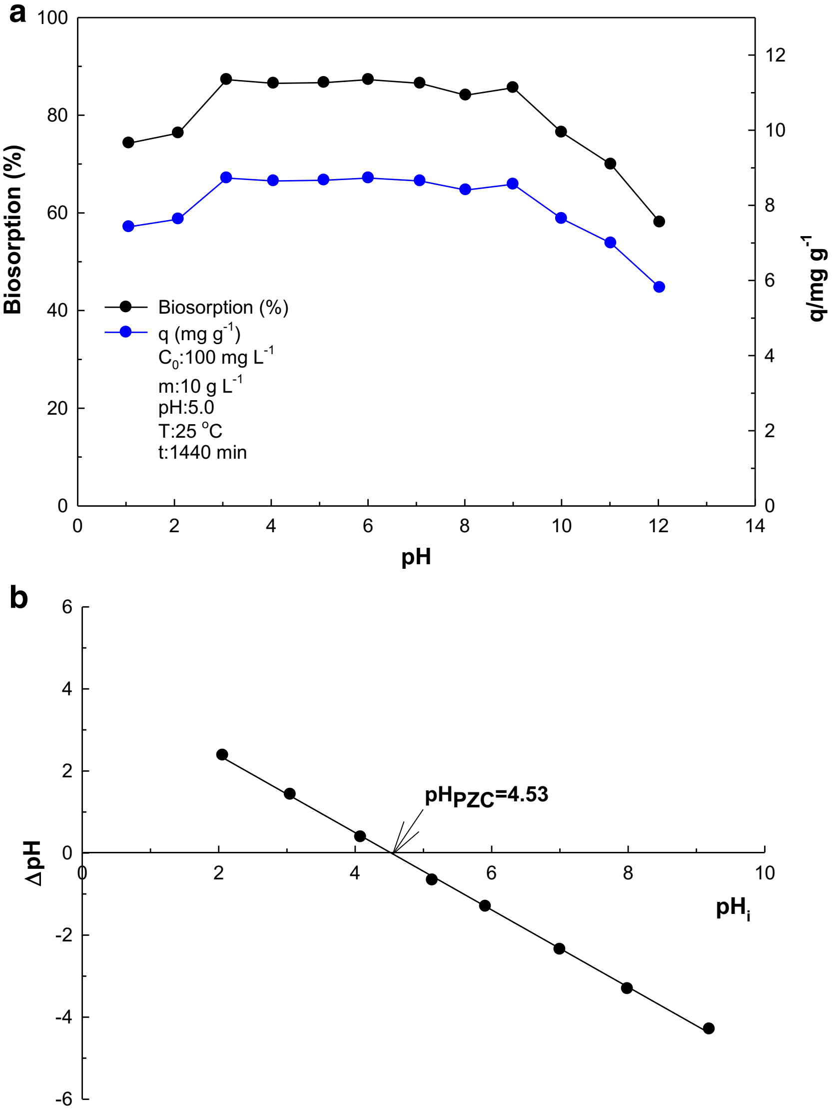


Fig. 3 **a** Effect of pH on the bio-sorption of BPA onto lichen bio-sorbent Fig. 3 **b** PZC plots of the lichen bio-sorbent in range of pH 2.0–9.0

bisphenolate anions and cause the electrostatic repulsion due to the negative charge of lichen biomass above pH_{pzc} of 4.53. Our results are in agreement with those of the sorption of BPA onto Fe_3O_4/GO and other sorbates reported in previous studies [31–34].

The solution pH at which the surface charge of the bio-sorbent becomes zero is defined as the point of zero charge (PZC). In order to determine the PZC values of the lichen bio-sorbent, 100 mg bio-sorbent was incubated for 24 h in pH solutions ranging from 1.0- to 12.0, and the equilibrium pH values were measured. The results are given in Fig. 3(b). The PZC of the lichen bio-sorbent was found to be 4.53. In other words, the surface charge of lichen bio-sorbent is positive below pH 4.53 and negative above pH 4.53. The surface charge of the lichen biomass becomes negative with increasing pH. It has been believed that BPA at optimal pH 5.0 is adsorbed onto the surface of lichen bio-sorbent by pH sensitive intermolecular hydrogen bonding, π-π stacking and hydrophobic interactions.

Finally, as the driving force in the bio-sorption process, it is clear that there are mechanistically two important factors affecting the bio-sorption of BPA employing the intermolecular hydrogen bonding, hydrophobic and π-π stacking interactions between the surface functional (hydroxyl, carboxyl, and carbonyl including aromatic benzene rings and long-chain alkyl groups) groups of the lichen biomass and the BPA selected as adsorbent and adsorbate, respectively [22, 25]. Since BPA contains π-electrons that can interact with the unsaturated π-electrons on main aromatic benzene moiety of the lichen biomass as well as bifunctional hydroxyl groups, π-π stacking interactions develop in the skeleton of the benzene rings of the BPA and the bio-sorbent.

Effect of bio-sorbent dosage

The effect of the bio-sorbent amount on BPA bio-sorption was studied in the range of 0.1–20 g L^{-1}. The results presented in

Fig. 4 showed that the bio-sorption yield increased as the amount of bio-sorbent increased due to the increased active areas on the surface of the bio-sorbent. Thus, the ions penetrate more easily into the bio-sorption areas. The maximum bio-sorption was found to be about 80% in the amount of 20 g L^{-1} bio-sorbent. As the number of bio-sorption active centers increased due to the increase in the amount of bio-sorbent, BPA bio-sorption onto the lichen biomass increased with the increase of bio-sorbent mass. Hydrogen bonds between hydroxyl groups in the structure of BPA and the effect of active phenolic and carboxylic groups in the structure of the lichen bio-sorbent were thought to be increased by the increase in the amount of bio-sorbent.

Bio-sorption isotherm models

The effect of initial BPA concentration on bio-sorption of BPA by lichen was based on the four common adsorption isotherms models called as Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Redlich-Peterson combining features of Langmuir and Freundlich isotherms. These isotherm models were applied to bio-sorption data, and the related parameters were derived. The adsorption isotherms used to evaluate the experimental data are shown in Table 1.

Figure 5 (a-b) shows the bio-sorption isotherms of BPA adsorption onto the lichen bio-sorbent and the parameters derived from these isotherms are given in Table 2. The suitability of experimental data with theoretical models was evaluated using R^2 values. When considered correlation coefficients of 0.982 and 0.984 in linearized forms, it was found that sorption isotherm best matched Langmuir and Redlich-Peterson models with two and three parameters, respectively, to explain the bio-sorption of BPA onto the lichen biomass. From the Freundlich model, K_f and the β parameters as a measure of capacity and intensity of bio-sorption were found to be 1.58 L mg^{-1} and 0.495, respectively where it indicates the relative distribution of the energy and heterogeneity of the sorbate sites. From Langmuir model, the maximum bio-sorption capacity was calculated as 10.4 mg g^{-1} and the K_L value was found to be 0.10 L mg^{-1}. The $E_{D\text{-}R}$ (kJ mol^{-1}) value gives information about sorption mechanism, physical or chemical. If it lies between 8 and 16 kJ mol^{-1}, the sorption process takes place chemically, while, $E_{D\text{-}R} < 8$ kJ mol^{-1}, the sorption process proceeds physically [35, 36]. From the D-R model, the bio-sorption energy was calculated to be 11.3 kJ mol − 1. This result suggests that the bio-sorption process of BPA onto the lichen biomass may be carried out by a mechanism being chemical in nature because the sorption energy lies within 8–16 kJ mol^{-1}.

Bio-sorption kinetics

The three most commonly kinetics models were used to evaluate the contact time dependence of the bio-sorption process. The bio-sorption kinetics of BPA onto lichen was described by the pseudo-first-order, pseudo-second-order and Elovich model for determining the nature (chemical or physical) of bio-sorption process while intra-particle diffusion, Bangham's pore diffusion and Boyd models are used for identifying the controlling step in adsorption process. Due to the bias resulting from linearization, attempts were also made to compare the kinetic and equilibrium models by the square sum of errors (SSE). SSE is represented by

$$SSE = \sum_{i=1}^{n} \frac{\sqrt{(qe,\exp - qe,cal)^2}}{N} \qquad (1)$$

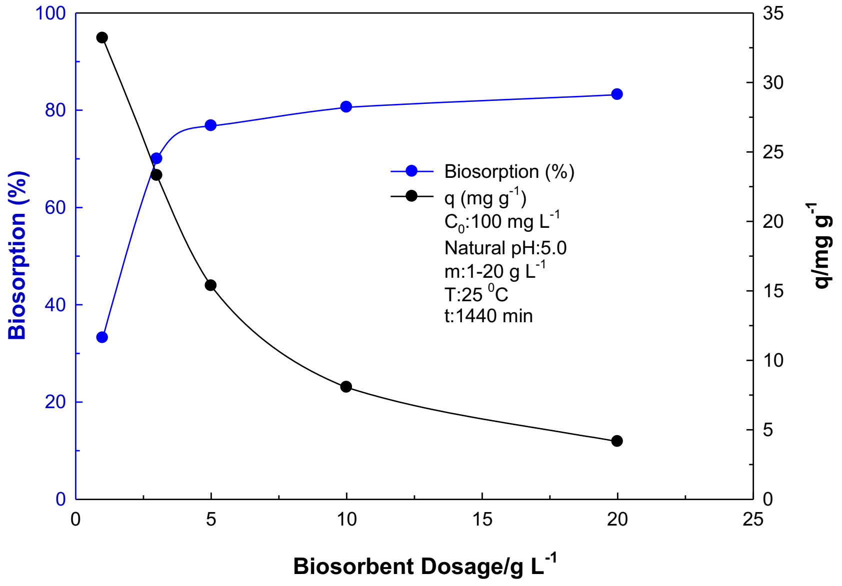
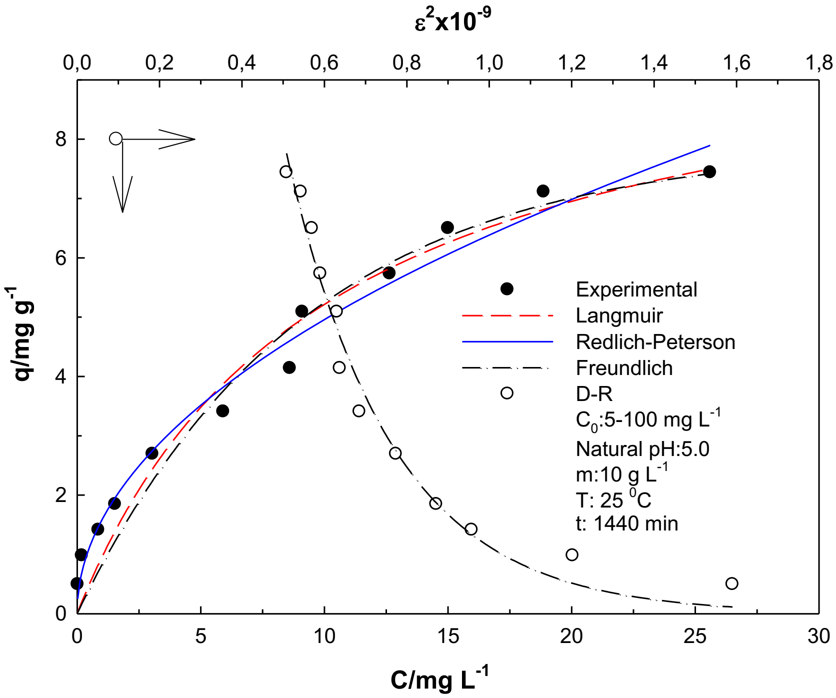


Fig. 4 The effect of bio-sorbent dosage on the bio-sorption of BPA onto lichen bio-sorbent

Fig. 5 The experimentally obtained bio-sorption isotherms of BPA onto lichen bio-sorbent



The effect of contact time on BPA bio-sorption by the lichen biomass is presented in Figs. 6 (a-c). The parameters derived from these kinetic models are given in Table 3. The equilibrium time for the bio-sorption of BPA onto the lichen biomass was found as 480 min.

From the regression coefficient (R^2) and the harmony of theoretically calculated Q_t and experimental Q_e values, it was concluded that the pseudo-second-order model with minimal error gave a good fit to the bio-sorption of BPA on the lichen bio-sorbent. The graph of the intra-particle diffusion model means that the bio-sorption process involves external diffusion and intra-particle diffusion stages, instead of a single linear passing through the origin. The first linear portion included the bio-sorption, which representing external diffusion and binding of BPA to active sites on the surface of the bio-sorbent. The second linear portion included the bio-sorption, representing intra-particle diffusion and binding of BPA by active sites distributed to pores of bio-sorbent. The bio-sorption process can be explained by intra particle diffusion model and pseudo second kinetic models. The surface of the lichen bio-sorbent firstly filled rapidly through chemical interactions, and then the intra particle diffusion proceeded slowly. Nevertheless, to ensure the accuracy and reliability of these findings, the further two kinetic models like Bangham's and Boyd models based on pore diffusion, and film diffusion and pore diffusion to elucidate the slowness of the rate-limiting step in the adsorption process were performed by plotting log log (c_0/(c_0-qm) and Bt as a function of logt and time, t, respectively. From the results obtained, it was observed that the two models supported each other in fast and slow rate-limiting steps with a better correlation coefficient than 0.953. In both regions, it was seen that the linear calibration curves did not pass through the origin with different slopes, and both film diffusion and pore diffusion relatively participated in the adsorption process of BPA, indicating that the mass transfer into the surface of the lichen biomass is realized by a complex mechanism [37].

In fact, two distinct regions can be clearly seen in Boyd's kinetic model: a first linear portion with the lower slope, from 20 min to 240 min, that represents film diffusion (R^2 values were found to be 0.981 for I. region and 0.996 for II. region), a second linear portion for a sorption period from 240 min to 480 min, that represents pore diffusion and a third linear portion that indicates the sorption–desorption equilibrium

Table 2 Langmuir, Freundlich, D-R and Redlich-Peterson isotherm parameters

Isotherm	Parameter	Value	R^2
Langmuir	X_L (mg g^{-1})	10.4	0.984
	K_L (L mg^{-1})	0.10	
Freundlich	K_F	1.58	0.946
	β	0.495	
D-R	X_{DR}	56.9	0.968
	-K_{DR}x10^9	3.92	
	E_{DR}/kJ mol^{-1}	11.3	
Redlich-Peterson	A ×10^9 (L g^{-1})	4.24	0.982
	B ×10^9 (L $mg^{-(1-1/A)}$)	2.68	
	g	0.505	

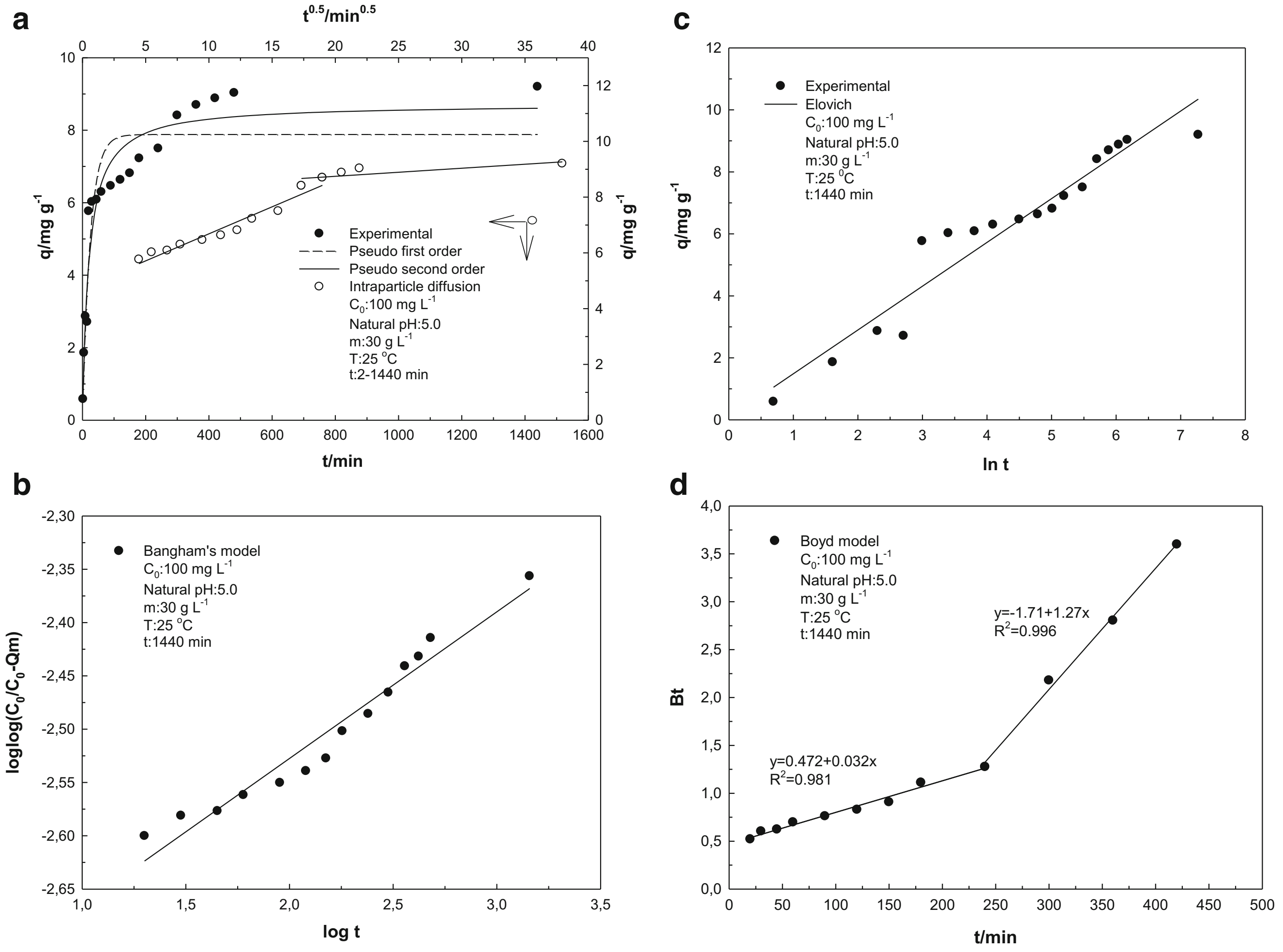


Fig. 6 Compatibilities of bio-sorption kinetics of BPA: (**a**) to pseudo first order, pseudo second order, and intra particle diffusion models Fig. 6 (**b**) Its compatibility to Bangham's model Fig. 6 (c) Its compatibility to Elovich model Fig. 6 (**d**) Its compatibility to Boyd model

Table 3 Bio-sorption kinetic parameters

Kinetic model	Parameter	Value	R^2	SSE
Pseudo-first-order	q_t/mg g^{-1}	9.19	0.878	7.28
	q_e/mg g^{-1}	7.88		
	$k_1 \times 10^3$/min^{-1}	40.4		
	Hx10^3/mg g^{-1} min^{-1}	318		
Pseudo-second-order	q_t/mg g^{-1}	9.19	0.931	2.61
	q_e/mg g^{-1}	8.72		
	$k_2 \times 10^3$/ mg^{-1} g min^{-1}	5.63		
	Hx10^3/ mg g^{-1} min^{-1}	428		
Intra particle diffusion	$k_i \times 10^3$/ mg g^{-1} $min^{-0.5}$	4.87	0.936	3.11
Bangham's model	k_0	-2803	0.953	–
	α	0.138		
Boyd model	D_i/cm^2 s^{-1}	$(3–17) \times 10^{-9}$	0.981	–
		$(1.21–6.76) \times 10^{-7}$	0.996	
Elovich model	α	1.489	0.929	4.02
	β	0.708		

From slope and intercept data obtained from Bt-t linearity plots in first and second regions where F is lower ($0<F<0.85$) and higher ($0.85<F<1$) than 0.85 as a function of time, respectively for particle size in range of 150–350 μm. The linear regression equations in I. and II. regions were $y = 0.472 + 0.032x$, R^2 : 0.981; and $y = -1.710 + 1.270x$, R^2 : 0.996; indicating that both linear curves do not pass through the origin. Values represent the minimum sum of square error (SSE)

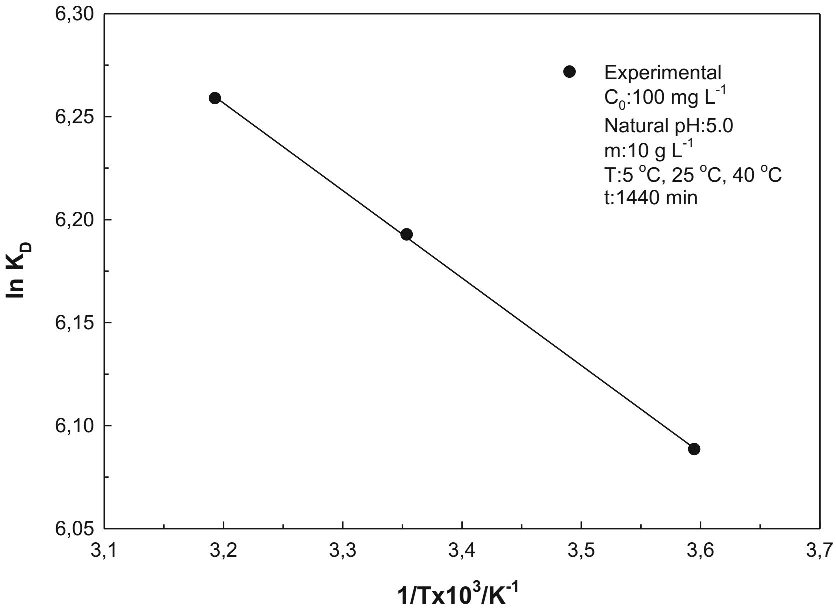


Fig. 7 The effect of temperature on the bio-sorption of BPA by lichen bio-sorbent

(herein, it was not presented in the text) with a slope near to zero. BPA sorption rate is relatively slow up to 240 min and at a rate increase between 240 and 480 min. The slow initial increase for the first region is due to the availability of free sites on the external surface based on film diffusion while with the extension of time (240–480 min) the BPA sorption decreased on the surface and took place within the pores. At this stage, the intra-particle diffusion of BPA into the pores, which is controlled with pore diffusion, determines the rate. In Fig. 6(c), it is also presented that the linear plots did not pass through the origin, suggesting that intra-particle diffusion proceeded with both film diffusion and pore diffusion is not the only rate-controlling step. Also, it is implied in literature [38] that the cause of the linear plots is not passing through the origin may be resulted from the difference in rate of mass transfer in the initial and final steps of bio-sorption. These results clearly indicated that neither the pore diffusion nor film diffusion is the only rate controlling step.

Bio-sorption thermodynamics

To explain the thermodynamic bio-sorption behavior of BPA by the lichen biomass, an experimental study was studied at temperatures of 5, 25 and 40 °C (Fig. 7). Thermodynamic parameters including enthalpy change (ΔH^o), entropy change (ΔS^o) and free energy change (ΔG^o) during the bio-sorption process were calculated using the equations in Table 1 and the results are presented in Table 4. In Fig. 8 (ln K_D-1/ T) the values of ΔH^0 and ΔS^0 were calculated from the slope of the graph and the cut-off, respectively. The value of ΔH^o, which is calculated as 3.53 kJ mol^{-1}, showed that the bio-sorption was endothermic. The value of ΔS^o was calculated as 63.3 $Jmol^{-1}$ K^{-1}, indicating an increase in the randomness of the bio-sorbent/solution interface during the bio-sorption process. Gibbs free energy value was calculated as −14.1, −15.4 and − 16.3 kJ mol^{-1} at 5, 25 and 40 °C, respectively. The negative Gibbs free energy value indicated that spontaneous of bio-sorption was possible. The BPA bio-sorption onto the lichen biomass was the tendency to spontaneously increase at higher temperatures.

Table 4 Bio-sorption thermodynamic parameters

ΔH^0/ kJ mol^{-1}	ΔS^0/ J mol^{-1} K^{-1}	ΔG^0/ kJ mol^{-1}	R^2
3.53	63.3	−15.4	0.999

Desorption efficiency

In this study, methanol, ethanol, dilute HCl and NaOH solutions (each one, 0.1 mol L^{-1}) were used for desorption of the BPA from the surface of the lichen bio-sorbent. In order to determine the recovery rates of the lichen biomass with desorption in Fig. 8, the experiments were repeated three times with the same bio-sorbent for the bio-sorption/desorption cycle. At the end of each experiment, the solutions were centrifuged at 5000 rpm for 10 min to ensure liquid-solid separation and the amounts of BPA in the equilibrium solution were detected at 287 nm utilizing UV-Visible spectrophotometer. From the results, it was observed that ethanol gave the best desorption efficiency (with a recovery rate of 86%) while the lowest recovery rate is obtained from elution with dilute NaOH (19%). So, ethanol was selected as a suitable desorption solvent for the regeneration of the lichen biomass, and used for further studies. Supporting existing results similar

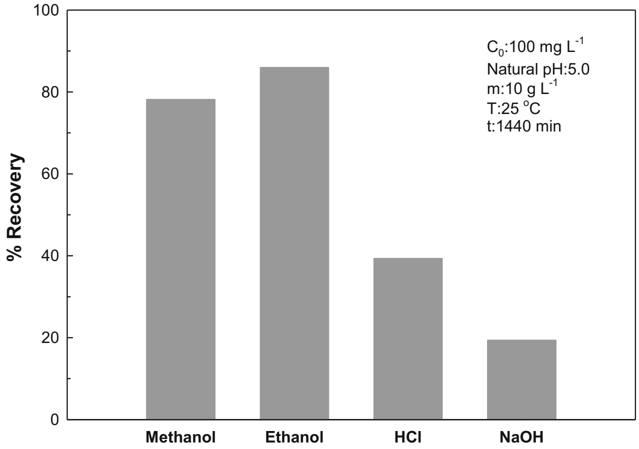


Fig. 8 The recovery rates of various solvents for desorption of BPA

results have been observed in the literature [19, 20] where the polar and nonpolar organic solvents such as ethanol, methanol, cyclohexane and toluene are efficiently used in desorption of BPA. Moreover, it has been implied in another study [21] that the desorption rate of BPA is significantly improved by using ultrasonic irradiation (within ultrasound power in the range of 17–100 W at 20 kHz) in presence of ethanol or methanol. The lichen biomass can be recycled at least eight times without the expense of adsorption capacities. After eight cycles, the adsorption capacity was around 82% with a decrease of 5.0% in the recovery rate. This reasonable and acceptable reusability performance indicates that the lichen biomass can be used in practical applications for the removal of BPA.

Comparison of the maximum sorption capacity of BPA on the lichen biomass with those of other bio-sorbents

A comparison has been made between the performances of the lichen biomass and other bio-sorbents reported in the literature for bio-sorption of BPA. The maximum sorption capacity obtained from the Langmuir model was used for comparison with those of different sorbents without modification and activation. As can be seen in Table 5, the maximum sorption capacity of the lichen biomass was comparable to that of the other bio-sorbent materials with no modification and activation, except for one [39]. As a result, the lichen biomass can be easily prepared at room temperature in terms of availability and easy accessibility of biomass and eco-friendly cleanup of the environment from low levels of BPA, and effectively used for bio-sorption of BPA at pH 5.0 by the synergy between hydrogen bonding and hydrophobic interaction. Because of these advantages, the lichen biomass can be directly used as a cheap, effective and alternative bio-sorption material in environmental cleanup. According to the obtained results, reasonable sorption capacity and a performance that can compete with other bio-sorbents in this work indicated that the lichen biomass was simple, easy to use and cost-effective bio-sorbent for removal of toxic BPA at ppm levels from aqueous solutions.

Conclusions

In conclusion, the lichen biomass with an excellent bio-sorption capacity for various emerging pollutants was efficiently used for bio-sorption of endocrine disruptor BPA. The lichen biomass without modification was thoroughly characterized using FT-IR, SEM, and charge of zero point measurements, suggesting that the bio-sorbent is an eco-friendly and easily accessible functional material with a positive and negative charge at lower and higher pHs than pH_{pzc}. The results also indicated that the material has the ability to form pH-sensitive hydrogen bonding interactions as well as weak van der Waals and $\pi-\pi$ stacking interactions with pollutants such as BPA. The important variables affecting the bio-sorption process were investigated in detail. The isotherm studies suggested that the Langmuir and Redlich-Petersen isotherm models with two and three parameters, respectively,

Table 5 Comparison of the maximum sorption capacity of BPA on the lichen biomass with those of other biosorbents

Biosorbent	pH, or pH_{pzc}	Temperature, °C	Max. sorption capacity, Q_{max}, mg g^{-1}	References
Orange albedo (*Citrus sinensis*)	4.5	25	82.36	[39]
Black tea leaves waste	7.0	15	18.25	[40]
Granular active carbon	7.0	15	16.26	[40]
Coconut shell, Durian peel, Coir pith, Banana bunches, and Coconut bunches	3,5,7,9	25	4.159, 4.178, 4.308, 4.532, 4.662	[41]
Fibric peat modified with and without HTAB	6.9	25	15.97, 21.15	[42]
Barley husk	3.0	25	15.26	[43]
The lichen biomass without modification	5.0	25	10.4	This study

HTAB: Hexadecyltrimethylammonium bromide best fit the data for BPA bio-sorption onto the active surface sites of the lichen biomass. The bio-sorption kinetics of BPA onto the lichen biomass was studied by pseudo-first order, pseudo-second order and intra-particle diffusion models, including Bangham's and Boyd kinetic models based on pore diffusion, and film and pore diffusions for control of mass transfer in the rate-limiting step. The results showed that the pseudo-second order model provided the best fit of the bio-sorption data for BPA. However, from Bangham's and Boyd kinetic models, because the linear plots do not pass through the origin, it was observed that neither film diffusion nor pore diffusion in control of mass transfer taking place in the solid-liquid interface is the only rate-limiting step. The negative ΔG° value indicated the spontaneous nature of the bio-sorption process, and the positive ΔH° value indicated that the bio-sorption process was endothermic in nature for BPA.

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Compliance with ethical standards

Conflict of interest The authors strongly declare that no scientific and/or financial conflicts of interest, exists with other people or institutions.

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