Article

Adsorption of Bisphenol A Using Dried Rice Husk: Equilibrium, Kinetic and Thermodynamic Studies

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Abstract

The adsorption of bisphenol A from an aqueous solution onto dried rice husk was investigated. Batch adsorption experiments were performed as a function of the pH, contact time, bisphenol A concentration, adsorbent dose and temperature. The concentration of Bisphenol A was measured by HPLC. The results showed that bisphenol A removal was highest at a solution pH value of 3, adsorbent dose of 4 g/L, and contact time of 75 min. The bisphenol A removal percentage decreased from 99.1 to 66.7%, when the bisphenol A concentration increased from 10 to 200 mg/L. The Langmuir isotherm and pseudo-second order kinetics provided the best fit for the experimental data. Thermodynamic parameters such as $\triangle G^0$, $\triangle H^0$ and $\triangle S^0$ were also evaluated and it was found that the sorption process was feasible, spontaneous and exothermic in nature. Overall, the studied absorbent can be used as an effective and low cost material to treat the industrial wastewater and aqueous solution containing phenolic compounds.

Keywords: Rice husk, Bisphenol A, Isotherm, Adsorption, Kinetics, Thermodynamics

1. Introduction

Bisphenol A [2,2-bis(4-hydroxyphenyl)propane] or BPA is one of endocrine-disrupting chemicals (EDCs) which it can threaten the human health[1]. Annually, 3,700,000 ton of BPA is produced in the world. The production of BPA is increasing due to increase of using the materials contained BPA which it can cause to release the large amount of BPA[2,3]. It is significantly useful in various industries to produce food and drink packaging, medical devices, food and beverage cans, and PVC pipes and it can be found in various component of environment[4-6]. As it has been reported by previous studies, the BPA can create the harmful effects on human health and environmental[7]. The reducing of fertility and increased incidences of breast, ovarian, and testicular cancers is only some of the adverse effects on human health[8]. Also, its acute toxicity for a number of freshwater and marine species has been proven[9]. Therefore, the BPA removal from water and wastewater should be considered as a major work to preserve the public health. Many techniques such as biological and physicochemical methods such as adsorption, chemical oxidation, advanced oxidation processes, and photocatalysis and membrane filtration have been used to BPA removal from water and wastewater[10,11]. Although the Activated carbon has been introduced as the best adsorbent to remove the BPA, however the available deficiency such as high cost shows the necessity of discovering the inexpensive and efficient alternative[12]. Various natural materials such as bark and wood chips[13], *Lemna minor*[14], bagasse[15], straw and rice husks[16], Canola[17], *Azolla filiculides*[18] and others have been used to remove BPA. The rice husk is one agricultural residue which can be used as low-cost adsorbentp[19]. Recently, the residues of rice husk are going to be greater and more available due to increase the tendency to consume the vegetable oils in Iran and the entire world[20,21]. The residues of rice husk have been used as adsorbent in several studies and have been indicated the acceptable results to remove the pollutants[22,23]. Therefore, the aim of this study was to assess: a) the ability of rice husk for BPA removal from aqueous solution, b) the effect of studied parameters including Contact time, pH, Adsorbent dose, temperatures and Initial BPA concentration, c) the isotherm, kinetic and thermodynamic studies.
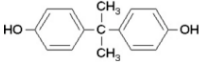
2. Material and Methods

2.1. Preparation of adsorbent

In this study, the rice husk was used as low cost natural or agricultural wastes for BPA removal from aqueous solutions. The rice husk was collected from research farm of Sari agricultural school. The stalks were washed several times with water to remove the contaminant, dried in the oven at 105 ℃ for 5 h. The biomass was then treated with 0.1 M HCl for 2 h followed by the washing with distilled water and then was oven dried at 105 ℃ for 3 h. After drying, adsorbent were

Table 1. Characteristics of Bisphenol A

Names	Molecular weight	λ_{max} (nm)	Molecular formula	Solubility in water	Structure
p,p'-isopropylidenebisphenol, 2,2-bis(4-hydroxyphenyl)propane	228.1 g/mol	225 nm	C_6H_5ClO	120 mg/L	

sieved to obtain particle size of 18 mesh prior to being used for adsorption studies.

The specific surface area of rice husk before use was determined by the BET-N2 method using an ASAP 2000 apparatus based on nitrogen adsorption-desorption isotherms at 77 K.

Treated rice husk biomass before and after use were examined using an environmental scanning electron microscopy (ESEM) instrument (Philips XL30 ESEM-TMP). The FTIR spectra (Nicolet 5700 Instrument, Thermo Corp, USA) were recorded in the range of 400~4,000 cm^{-1} to find out the information regarding the bending vibrations and the stretching of the functional groups which are responsible for the adsorption process.

2.2. Preparation of BPA solution

The BPA used in this study obtained from a Merck company in Germany and used without further purification. The chemical structures and general data are displayed in Table 1, respectively. The BPA stock solutions were prepared by dissolving accurately weighted BPA in distilled water to the concentration of 1,000 mg/L and the experimental solutions concentrations were obtained by dilution.

2.3. Batch adsorption experiments

By reviewing of performed studies, it was discovered that contact time, pH, initial BPA concentration and adsorbent dose can attribute as the effective parameter on the adsorption process. It is reported that the BPA concentration in textile effluent is between 10 and 200 mg/L; therefore, the initial BPA concentration was selected 10, 25, 50, 75, 100, 150 and 200. The effect of adsorbent dosage, contact time, pH and temperatures were studied in a range of (0.5~8 g/L), (10~150 min), (3~11) and 273~333 K respectively. The pH of BPA solution was regulated by 0.1 M NaOH and HCl. The experiments in a batch system were carried out in a 250 mL Erlenmeyer flask. In each adsorption experiment, certain amount adsorbent was added to the Erlenmeyer with known concentration of BPA. The samples were mixed by shaker with 180 rpm for 120 min. Then the samples were centrifuged at 3,600 rpm for 10 min. This study was done according on optimization of each parameter. For example to obtain the optimum contact time, all parameters assumed constant except contact time. The contact time was varied between 10 and 150 min and the time with maximum BPA removal is considered as optimum contact time. This time was constant in next steps. This is continued in the next experiments to find the other optimum parameters. The initial and equilibrium concentration of BPA in solution was determined by HPLC. In the HPLC analysis, the mobile phase was a mixture of 50 m Ammonium acetate and methanol (50 : 50, v/v). The flow rate was 1.0 mL/min, the detection wavelength was 225 nm, and the injection volume was 10 mL. The BPA removal

percentage (R) and the amount of adsorbed BPA on adsorbent, q_e (mg/g), were calculated by equations 1 and 2, respectively[24,25].

$$R = \frac{(C_0 - C_e) \times 100}{C_0} \tag{1}$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \tag{2}$$

where q_e is the amount of adsorbed BPA per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and the equilibrium concentrations of BPA solution (mg/L), respectively. V is the volume of the BPA solution (L), and M is the mass of the adsorbent. Each sorption experiment was carried out several times and average value is presented.

3. Results and Discussion

The surface area of dried rice husk was 94.5 m^2/g, in which it indicated that the modified rice husk area have relatively good ability to remove the pollutants. Fourier transform infrared spectroscopy (FTIR) is often used to examine characteristic functional groups that make the adsorption behavior possible. The FTIR of sesame leaf before adsorption of BPA is shown in Figure 1(a) and that of sesame leaf after adsorption in presented in Figure 2(b). As can be observed from Figure 1(a), the infrared spectrum displayed a large number of adsorption peaks, which indicated the presence of different types of functional groups in the biosorbent[26]. The broadband peak at 3,412 cm^{-1} was attributed to the stretching vibration of bonded hydroxyl groups on the surface of sesame leaf[27]. The peak at 2,921 cm^{-1} is attributed to the symmetric and asymmetric C-H stretching vibration of aliphatic acids. The precursor had C=O stretching of aldehyde group peaks located at 1,738 cm^{-1}. The peak at 1,662 cm^{-1} is due to asymmetric stretching vibrations of C=O and the peaks observed at 1,512, can be assigned to C=C vibration in aromatic rings[28]. The other prominent peaks are due to NH$_2$, C=O (1,459 and 1,395, 1,065 and 875 cm^{-1}, respectively) groups. After BPA adsorption there is remarkable shift in the positions of -OH, C=O and -C-C- group peaks, which indicates BPA binding mostly to -OH and C=O groups. The changes in FTIR spectra confirm the complexation of BPA with the functional groups present in the adsorbents. Dried rice husk was also examined before and after use using environmental scanning electron microscopy. Figure 2(a) clearly shows the pore textural structure of dried rice husk before use. However, as shown in Figure 2(b), clear pore textural structure is not observed on the surface of dried rice husk after use which could be due to either agglomeration on the surface or the incursion of BPA into the pores of dried rice husk biomass.
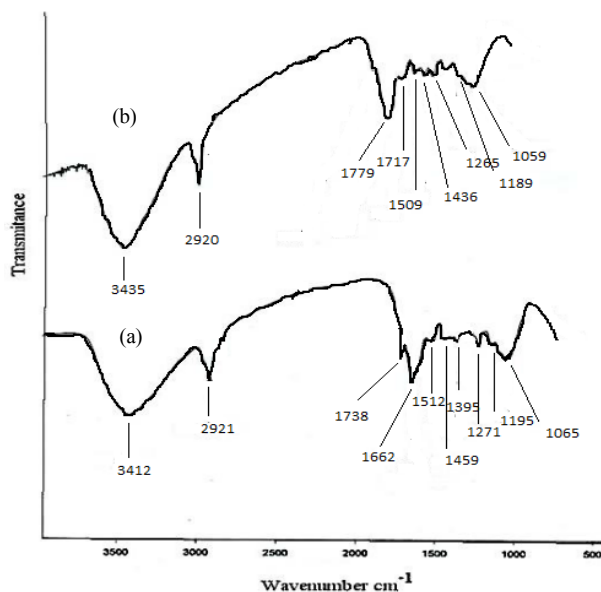
Figure 1. FT-IR spectra of rice husk (a) before and (b) after BPA adsorption.
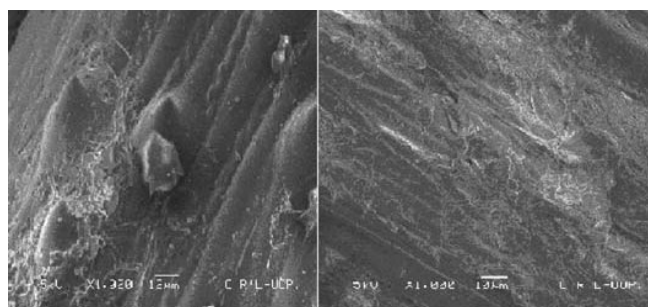

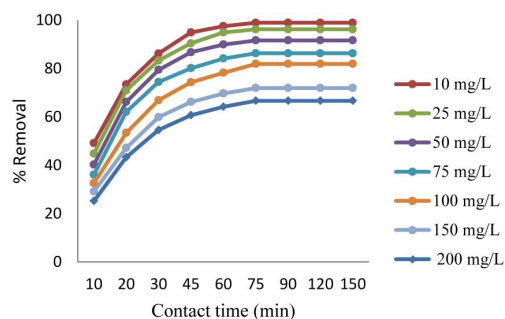Figure 2. SEM image of rice husk (a) before (b) after used.

Figure 3. Effect of contact time and initial BPA concentration (pH = 3, Biomass dose: 4 g/L).

3.1. Effect of contact time and initial BPA concentration on adsorption

The plot of removal efficiency at different contact time, as shown in Figure 3 and the result reveals a two-stage kinetic process: a rapid initial adsorption during the first 45 min, followed by a longer period of much slower uptake. The maximum removal efficiency was observed after 75 min, which was chosen as the experimental contact time for this study. The effect of initial BPA concentration at different contact
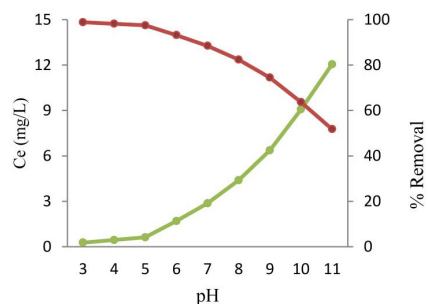

Figure 4. Effect of pH on adsorption (Con = 25 mg/L, Contact time = 75 min, dose: 4 g/L).

time (10~120 min) on the sorption of BPA at pH 3 for dried biomass powder is presented in Figure 1. The increase in adsorption efficiency by increasing the contact time can be due to the existence of abundant vacant active sites in the adsorbent surface. However, with increase in contact time, the availability of BPA to the active sites on the adsorbent surface would be limited, which makes the adsorption efficiency to reduce. Some studies described similar phenomenon for BPA adsorption on the different adsorbents. For example, the result of the study of Zazouli et al.[29] showed that the adsorption of BPA by Red mud reached the equilibrium state at 90 minutes, while Girish et al.[30] showed that the adsorption of Phenol on agricultural waste reached the equilibrium state at 75 min. The % removal decreased from 99.1 to 66.7 with the increasing of initial BPA concentrations in the range of 10~200 mg/L. The decreasing removal efficiency due to saturation the vacant sites on the adsorbent surface in higher BPA concentrations[6]. As respects for a specified amount of an adsorbent, adsorption sites is constant, thus by increasing the initial BPA concentration, removal efficiency is reduced. Furthermore, by increasing the initial BPA concentration, was created repulsive between BPA molecules and was prevented from BPA adsorption on the adsorbent[24]. In 2007, Wang et al. adsorption of 3-chlorophenol on rice-straw were investigated. The results of this study revealed that by increasing the initial concentration of the 3-chlorophenol, the rate of adsorption is reduced[26]. Rengaraj's study showed that by increasing the concentration of Phenol compounds of 25~100 mg/L, the removal efficiency of 95.6~69.2% was decreased[31]. The efficiency of bentonite for the removal of the phenol from aqueous solution by the Banat et al. was investigated. With increasing initial phenol concentration of 25~100 mg, the removal efficiency was decreased from 97.2% to 59.4%[25].

3.2. Effect of solution pH

The pH has identified as a critical parameter in the adsorption process. To study the influence of pH on the adsorption capacity of rice husk for BPA, experiments were performed at BPA initial concentration of 25 mg/L using different initial solution pH values, changing from 3 to 11. Figure 4 shows that the BPA removal was maximum and unaffected when the initial pH of the BPA solution was in the range of 3~5. At acidic pH, BPA are neutralized, whereas the absorbent surface is surrounded by hydronium ion. This results in an increase in surface tension between BPA and binding sites on the adsorbent sur-
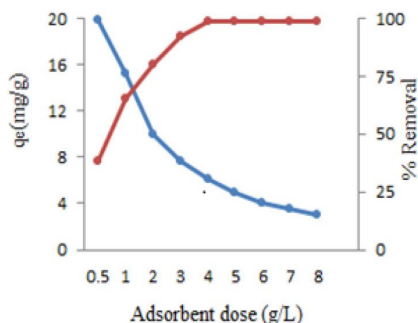
Figure 5. Effect of adsorbent dose (Contact time = 75 min, pH = 3, Con: 25 mg/L).

face[27]. At alkaline pH, along with increase in the percentage of ionized species, the number of negative charged sites on the adsorbent surface increased. Thus, adsorption will decrease due to electrostatic desorption between the negative surface of the absorbent and BPA anions[12]. The result of this study is in line with the result obtained by Gulbeyi on the removal of phenol using beet pulp[28].

3.3. Effect of adsorbent dose

The amount of adsorbent on the efficiency of adsorption was also studied (Figure 5). The percentage adsorption increased from 43~99.1% when adsorbents doses were increased from 0.5~4 g L^{-1} for adsorbent, but at the same time adsorption density decreased from 19.9~3.1 mg g^{-1}. Zazouli et al.[29] showed that removal bisphenol increased with increasing amount of adsorbent due to availability of larger surface area to absorb. Dong et al.[27] reported that the removal efficiency of BPA was raised with increase in the adsorbent dosage. However, a decrease in the adsorption capacity with an increase in the adsorbent dosage is probably due to instauration of the active sites on the adsorbent surface during the adsorption process[32,33].

3.4. Isotherm studies

The experimental data obtained from the adsorption of BPA onto dried rice husk was analyzed by isotherm models. The obtained data from this Isothermic study helps to successful design of adsorption system. Four well-known isotherm models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were applied and their applicability for BPA adsorption was investigated.

3.4.1. Langmuir isotherm

The linear form of the Langmuir isotherm can be represented by the following equation[34,35]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_m the maximum monolayer adsorption capacity (mg/g) and K_L is the Langmuir constant related to rate of adsorption.

3.4.2. Freundlich isotherm

The Freundlich equation is also often used as an empirical relationship between the concentration of a sorbate on the surface of an adsorbent and the concentration of the sorbate in the solution at equilibrium. The Freundlich equation is based on the hypothesis of multi-layer biosorption and the linear form is given by the following equation. The linear equation is expressed as follows[36,37]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where, K_f and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Generally, the adsorption capacity of an adsorbent for a given adsorbate enhances with an increase in K_F.

3.4.3. Tempkin isotherm

Tempkin considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The linear form of Tempkin isotherm is[38,39]:

$$q_e = B \ln A + B \ln C_e \tag{5}$$

where $B = RT/b$, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant and B is corresponding to the heat of sorption.

3.4.4. Doubinin-Radushevich (D-R) isotherm

D-R model is a more generalized model as compared to the Langmuir isotherm. This model is based on the fact that there is no homogeneous surface or constant adsorption potential. The linear form of (D-R) isotherm model can be seen below[40]:

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{6}$$

where K is a constant corresponding to the biosorption energy, q_m the theoretical saturation capacity and ε is the Polanyi potential which is calculated from equation below[41]:

$$\varepsilon = RT \ln (1 + 1/C_e) \tag{7}$$

where R (kJ mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. E was calculated from the K value by the following relation[42]:

$$E = 1 / (2K)^{\frac{1}{2}} \tag{8}$$

The results and correlation coefficients for isotherms model are presented in Table 2. By comparing the correlation coefficients R^2, it can

Table 2. Adsorption Isotherms Constants for the Removal BPA onto Rice Husk Biomass

Temp. (°K)	Langmuir model			Freundlich model			Temkin model			D-R			
	q_m	K_L	R^2	n	K_F	R^2	B	A	R^2	q_m	K	E	R^2
273	22.45	0.014	0.996	3.96	2.89	0.901	21.85	1.14	0.829	14.4	1.95	0.141	0.911
293	24.15	0.028	0.998	3.24	4.17	0.882	26.19	0.982	0.798	17.5	2.44	0.325	0.922
313	25.98	0.044	0.994	2.65	5.39	0.864	30.71	0.723	0.837	19.2	2.96	0.498	0.902
333	27.12	0.071	0.997	1.98	6.45	0.881	35.47	0.569	0.852	21.8	3.45	0.633	0.936

Table 3. Kinetic Parameters for BPA Adsorption onto Dried Rice Husk

C_o (mg/L)	Pseudo second-order model			Pseudo first-order model			Intraparticle diffusion		
	k_2	R^2	q_e (mg/g)	K_1	R^2	q_e (mg/g)	K	C	R^2
25	0.033	0.995	6.34	0.24	0.828	3.25	1.17	5.45	0.912
50	0.064	0.997	12.29	0.035	0.864	7.84	2.89	3.71	0.904
100	0.091	0.999	21.45	0.061	0.893	16.14	4.11	4.46	0.887
200	0.114	0.998	34.81	0.093	0.842	27.68	6.65	2.69	0.926
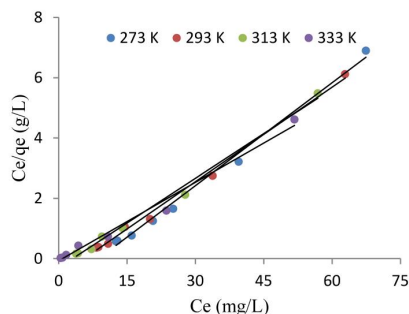
Figure 6. Langmuir adsorption isotherm of BPA onto rice husk at different temperatures.

Figure 7. Pseudo-second-order kinetic plot for the removal of BPA by rice husk.

be seen that the experimental equilibrium sorption data are better described by the Langmuir model than by the other models. Figure 6 shows a linear relationship of C_e/q_e versus C_e using experimental data obtained, suggesting the applicability of the Langmuir model (R^2 0.994). As it can be observed the correlation coefficient (R^2) of Langmuir isotherm was greater than models which it indicates that the obtained data from the isotherm studies is better described by the this model. The Langmuir isotherm model assumes that a monolayer adsorption exists on the adsorbent surface with a finite number of identical sites that all sites are energetically equivalent, and that there is no interaction between the adsorbed molecules and homogeneous distribution of active sites on the surface of rice husk. Similar results were reported by Dursun et al.[43]. The results of their study indicated that adsorption of phenol follows the Langmuir isotherm model for modified beet pulp. Rubín et al.[44] studied the removal of phenolic compound using brown alga *Sargassum muticum*. In their study the adsorption plots fitted very well with Langmuir isotherm model in temperature of 25 ℃.

3.5. Kinetic studies

In order to examine the mechanism and rate-controlling step in the overall adsorption process, three kinetic models, pseudo-first-order,

pseudo-second-order and intra-particle diffusion, are adopted to investigate the adsorption process[45,46]:

$$\text{Pseudo-first order: } \mathrm{Ln}\,(q_e - q_t) = \ln(q_e) - \frac{K_1 t}{2.303} \tag{9}$$

$$\text{Pseudo-second order: } \frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

$$\text{Intra-particle-diffusion: } q_t = kt^{0.5} + C \tag{11}$$

The K_1 and K_2 are rate constants of pseudo-first order and pseudo-second order of adsorption kinetic, respectively. q_e is amount of adsorption at equilibrium. K_i is the intra-particle diffusion rate constant. The kinetic parameters for the sorption of BPA on rice husk are summarized in Table 3. Based on the findings of this study, the adsorption of BPA follow the pseudo second-order kinetic. The q_e and K_2 values can be obtained from the slope and intercept of plots of t/q_t versus t which are depicted in Figure 7. The good linear plots of t/q_t versus t at different concentrations with the correlation coefficients (R^2) higher than 0.997 suggest that adsorption of BPA onto rice husk biomass fol-

Table 4. Thermodynamic Parameters for the Adsorption of BPA on Rice Husk

T (K)	$\triangle G^0$ (kJ/mol)	$\triangle H^0$ (kJ/mol)	$\triangle S^0$ (kJ/mol K)
273	-8.22		
293	-10.45	-21.72	-3.45
313	-13.88		
333	-15.36		

lows the pseudo second order kinetic model. Mahvi *et al.* reported that the adsorption of phenol by rice husk ash follow the pseudo second-order kinetic[34]. In another study, Aravindhan *et al.* investigated the efficiency of modified green macro alga in the removal of phenol. The results showed that the removal of phenol follow the pseudo second-order kinetic[47]. Achak *et al.* study showed that phenolic compounds removal by activated carbon made from banana peel follow the pseudo second-order kinetic[35].

3.6. Thermodynamic studies

Thermodynamic parameters such as standard free energy change ($\triangle G^0$), standard enthalpy change ($\triangle H^0$) and standard entropy change ($\triangle S^0$) can be calculated using the following equation[48,49]:

$$\triangle G^0 = -RT\, LnK_L \tag{12}$$

$$\triangle G^0 = \triangle H^0 - T\triangle S^0 \tag{13}$$

$$Ln(K_L) = \frac{\triangle S^0}{R} - \frac{\triangle H^0}{RT} \tag{14}$$

where K_L is the equilibrium constant, R is the gas universal constant (8.314 J/mol K) and T is the absolute temperature. The values of $\triangle H^0$ and $\triangle S^0$ are determined from the slope and the intercept of the plots of log K_L versus $1/T$. Table 4 presents the thermodynamic parameters at various temperatures. The estimated values of $\triangle G^0$ for adsorption BPA onto rice husk were -8.22, 10.45, 13.88 and 15.36 kJ/mol, respectively, at 273, 293, 313 and 333 K, which are rather low. The negative values of $\triangle G^0$ of the adsorption confirmed that the adsorption of BPA onto rice husk was feasible and spontaneous. Generally, the range of free energy values ($\triangle G^0$) for physisorption is between -20 and 0 kJ/mol, while chemisorption is between -80 and -400 kJ/mol[50-52]. This further indicated that the adsorption of the BPA onto rice husk was by physisorption. The change in adsorption standard enthalpy ($\triangle H^0$) for BPA adsorbed onto rice husk was -21.7 kJ/mol, indicating loose bonding between the BPA and rice husk since BPA was adsorbed and penetrated into the interlayer space of adsorbent, indicating that the adsorption process was exothermic. The adsorption of BPA onto rice husk can be concluded to be via physicosorption since the change in the standard enthalpy is less than 40.0 kJ/mol. The standard entropy change ($\triangle S^0$) for BPA adsorbed onto rice husk was -3.45 J/mol. The negative value of S0 suggested a decrease in degree

of freedom of the adsorbed BPA. Similar results were reported in the literature for the adsorption of BPA by Red mud[29].

4. Conclusions

The efficiency of Bisphenol A removal from aqueous solution by dried rice husk as a natural adsorbent was evaluated. The effect of parameters such as contact time, pH, Bisphenol A concentration, adsorbent doses and temperature were analyzed. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The experimental data yielded excellent fits within the following isotherms order: Langmuir, Dubinin-Radushkevich, Freundlich, Temkin, based on its correlation coefficient values. The thermodynamic analysis indicates that the system is spontaneous and exothermic. The suitability of the pseudo first and second order equations and intra particle diffusion kinetic model for the sorption of BPA onto rice husk is also discussed. The pseudo second order kinetic model agrees very well with the dynamical behavior for the adsorption of BPA onto rice husk for different initial BPA concentrations over the whole range studied. The rice husk appeared to be suitable for the removal of BPA from aqueous solutions.

Acknowledgements

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