



## Kinetics, Isotherm and Thermodynamics Studies on Bisphenol A Adsorption using Barley husk

Davoud Balarak\*

Department of Environmental Health, Health Promotion Research Center, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran

**Abstract :** The aim of this study is to investigate the possibility of barley husk biomass as an alternative adsorbent for bisphenol A (BPA) removal from aqueous solution. Effect of various parameters such as Contact time, pH, temperature, initial BPA concentration and adsorbent dosage has been carried out in this study. Isotherm studies were conducted on a laboratory scale and the data evaluated for compliance with Langmuir, Freundlich, Tekmin and Dubinin-Radushkevich isotherm models. Equilibrium data fitted well with the Langmuir model. The optimum conditions for the removal of BPA within the experiment range of variables studies were 10 mg/L of initial BPA concentration, 5 g/L of adsorbent dose, pH value of 3 and 90 min of contact time. Under these conditions the maximum removal efficiency was 98.9%. The Pseudo-first order, pseudo second order and intraparticle diffusion models were used to describe the kinetic data. The data were best fitted with pseudo second order kinetic model. Thermodynamic parameters were also evaluated and it was found to be spontaneous, endothermic and physical adsorption in nature.

**Keywords:** Bisphenol A, Biosorption, Barley husk, Equilibrium isotherms.

### Introduction:

Bisphenol A (BPA, 2,2-bis (4-hydroxyphenyl)) is an endocrine disrupting chemical has been widely used for the production of polycarbonate plastics (PC), epoxy resins, plastic packaging, dental sealants and water pipes(1-3). Analysis of BPA in urine samples showed that BPA is present in over 93% of the US population(4). Upon exposure to heat, acid or base, ester bonds that link the BPA monomers in these plastic or resin materials will be hydrolyzed, thus releasing BPA into the environment(5, 6). The concern about BPA has risen in that BPA has estrogenic effect on animals at low doses(7). More importantly, BPA can possibly cause breast cancer(8, 9). It has been recently demonstrated that BPA can leach out of these materials and contaminate the environment(10-12). More than one million tons of BPA are annually produced in the world(13). As a result, BPA is often detected in municipal and industrial wastewaters, sewage sludge and natural waters and sediments(14, 15). Due to its high bioactivity, ubiquitous nature, toxicity even at very low concentrations and persistence in water, it appears very important to develop efficient methods to reduce the presence of BPA in the environment and especially in aquatic systems(16, 17). Various methods like chemical, biological, Fenton, nanofiltration membrane and photocatalytic procedures have been used in the removal of Phenolic compounds in recent years(18, 19). But many kinds of Phenolic compounds cannot be completely eliminated by some methods, which in fact caused incomplete degradation products with higher endocrine disrupting action(20). Hence, it is urgent to develop a rapid and efficient treatment for the removal of phenolic compounds. Adsorption is one of the simplest and widely used methods that can be applied to removal micropollutants from water(21). Adsorption potential of selected activated carbons were tested and found that BPA was effectively

removed from aqueous solution(22, 23). However, the problem associated with the activated carbon decrease the attraction of its application(24). Therefore, the researchers are trying to find a low-cost and effective adsorbent. Recently, the various natural material such as Red mud, Banana peel, Apple residues, Orange peel, Azolla and etc have been used as effective adsorbents to remove the organic pollutants(19, 25).

The barley husk is one agricultural residue which can be used as low-cost adsorbent(26). Recently, the residues of barley 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(27, 28). The residues of barley husk have been used as adsorbent in several studies and have been indicated the acceptable results to remove the pollutants(29, 30).

The aim of the study was: (1) investigation of barley husk ability to remove the BPA from aqueous solution, (2) fitting four kinetic models to analyze the experimental data, (3) determination of adsorption behavior of BPA, (4) determination of impact of solution pH, contact time, initial BPA concentration and biomass dosage on sorption.

## Material and methods:

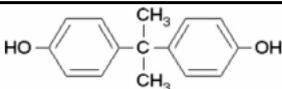
### 2.1. Preparation of Adsorbent

In this study, the Barley husk was used as low cost natural or agricultural wastes for BPA removal from aqueous solutions. The stalks of Barley husk (C) were collected from research farm of Tabriz agricultural school. The stalks were washed several times with water to remove the contaminant, dried in the oven at 105°C for 5 h. The biomass were then treated with 0.1M HCL for 2 h followed by the washing with distilled water and then was oven dried at 105°C for 3 h. After drying, adsorbent were sieved to obtain particle size of 18 mesh prior to being used for adsorption studies.

### 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 1000 mg/L and the experimental solutions concentrations were obtained by dilution.

**Table 1: characteristics of bisphenol A**

Structure	Solubility in water	Molecular formula	$\lambda_{\max}$ (nm)	Molecular weight	names
	120 mg/L	C <sub>6</sub> H <sub>5</sub> ClO	276 nm	228.1g/mol	<i>p,p'</i> -isopropylidenebisphenol, 2,2-bis (4-hydroxyphenyl)propane

### Batch adsorption experiments:

All experiments were carried out with biosorbent samples (5 g/L) at 25°C in 50 ml beakers in an IKA magnetic stirrer operating at 200 rpm to elucidate the optimum conditions (pH, contact time and initial BPA concentration). Before analysis of the BPA concentration, samples were centrifuged at 3600 rpm for solid-liquid separation. Finally, the residual concentrations were measured by Uv-visible (DR5000) in  $\lambda_{\max}$  of 276 nm. The BPA adsorption capacities of biosorbent were determined at a certain time intervals (10, 20, 30, 45, 60, 75, 90, 120 and 150 min). The effect of pH on biosorption was studied by adjusting BPA solutions (25 mg/L) to different pH values (3–11) and agitated with 5 g/L of biosorbent for 90 min. The BPA solutions were adjusted to the required initial pH values with the addition of HCl or NaOH (0.1 M). BPA adsorption experiments were also accomplished to obtain isotherms at temperature (20 °C) and to a range of 10–100 mg/L BPA concentrations. The amount of BPA adsorbed by biosorbent,  $q_e$  (mg/g), was calculated by the following mass balance relationship(31):

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium BPA concentrations in solution, respectively (mg/g),  $V$  the volume of the solution (L) and  $W$  is the mass (g) of the adsorbent used.

## Results and discussion:

### Effect of contact time and initial BPA concentration on biosorption

The plot of removal efficiency at different contact times shown in Fig. 1 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 90 min, which was chosen as the experimental contact time for this study. The rapid adsorption observed during the first 45 min was probably due to the abundant availability of active sites on the barley husk biomass surface, and with the gradual occupancy of these sites, the adsorption became less efficient(32). Similar behaviour regarding the absorption of Phenol on beet pulp was observed by Gulbeyi(20).

The effect of initial BPA concentration at different contact time (10-150 min) on the sorption of BPA at pH 3 for dried biomass powder is presented in Fig. 1. The %removal decreased from 98.1 to 72.9 with the increasing of initial BPA concentrations in the range of 10–100 mg/L, but adsorption capacity ( $q_e$ ) increased from 1.1 to 15.26 mg/g. Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent(33). First, the adsorbate migrates through the solution, i.e., film diffusion, followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle. This phenomenon takes relatively long contact time. Sui et al(22). investigated the effect of initial concentration of Phenol on the biosorption of rice husk. The  $q_e$  increased from 1.41 to 16.64 mg/g with an increase in the Phenol concentration from 10 to 150 mg/L.

The pH of aqueous solution has been known as the most important variable affecting BPA adsorption onto biosorbents. Fig. 3 clearly shows that dried barley husk biomass also exhibited maximum BPA removal within the pH range of 3-5. A similar trend of pH effect was observed for the adsorption of phenol on azolla filiculoides and lemna minor(19). Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate. BPA as a weak acid compound with  $pK_a \approx 9.5$  is dissociated at  $pH > pK_a(1)$ . Therefore, the adsorption decrease at high pH values due to ionization of adsorbate molecules. The reason could be also due to the electrostatic repulsions between the negative surface charge and the BPA anions in solution(34). While at acidic pH, the percentage removal was higher because BPA was undissociated and the dispersion interaction predominated.

The increase of adsorbent dosage from 1 to 5 g/L causes an increase adsorption rate of 45% to 98.9. This is due to the fact that, increase in adsorbent dosage increase area available for adsorption(35). At lower adsorbent doses, increase in removal is proportional to the increase in adsorbent dose. At a Dianati et al(36). observed that the amount of phenol adsorbed per unit weight of adsorbent decreased with increase in adsorbent mass. The amount of phenol adsorbed decreased from 18.11 to 2.5 mg/g for an increase in adsorbent concentration from 1 to 8 g/L, whereas the percentage removal increased from 39.25% to 94.3%. They the decrease in the amount of phenol adsorbed with increasing adsorbent mass was due to adsorption sites remaining unsaturated during the adsorption reaction(30). This was due to the fact that as the dosage of adsorbent was increased, there was a less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent.

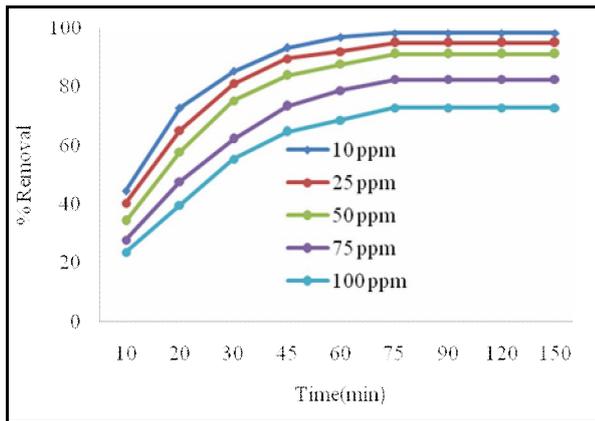


Fig. 1. Effect of contact time and initial BPA concentration (pH =3, Adsorbent dosage 5 g/L)

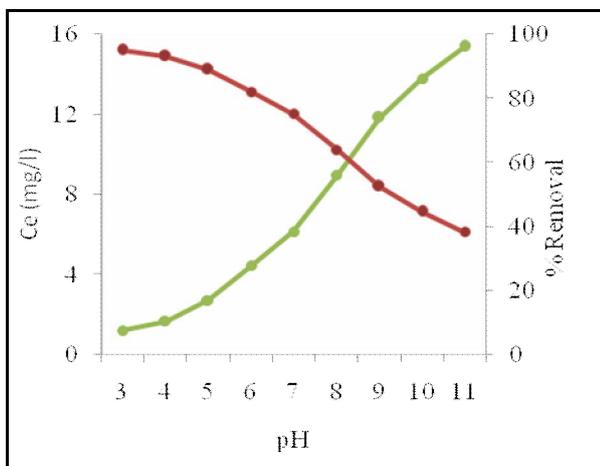


Fig. 2. Effect of pH on BPA removal efficiency (C<sub>0</sub> = 25 mg/L, adsorbent dose of 5 g/L, contact time = 90 min)

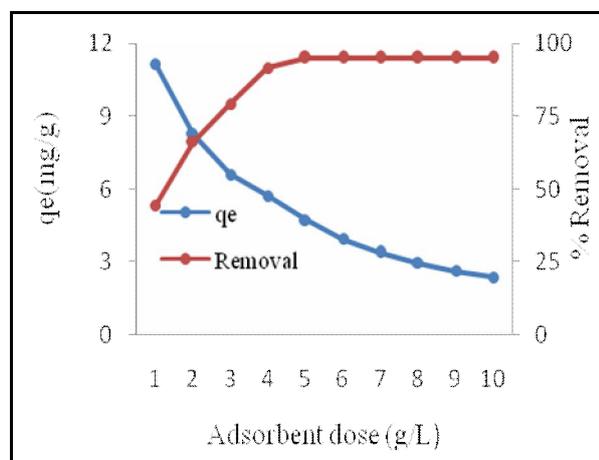


Fig. 3. Effect of biomass dose on BPA biosorption (C<sub>0</sub> = 25 mg/L, pH=3 Contact time=75 min)

**Adsorption kinetics**

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[52-54].

The pseudo-first-order equation can be expressed as the following equation(25, 37):

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{K_1}{2.303}t$$

Where q<sub>e</sub> and q<sub>t</sub> are the biosorption capacity (mg/g) at equilibrium and time t, respectively, k<sub>1</sub> is the constant rate (L min<sup>-1</sup>) of pseudo first order kinetic model.

The values of k<sub>1</sub>, calculated q<sub>e</sub>, experimental q<sub>e</sub> and R<sup>2</sup> are presented in Table 2. Furthermore, the experimental values of q<sub>e,exp</sub> (mg/g) are far from the calculated q<sub>e,cal</sub> (mg/g). This suggests that the pseudo-first-order kinetic model is not suitable to describe the adsorption process.

The pseudo-second order kinetic model can be described as follows(38, 39):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t}$$

Where  $q_e$  is the biosorbed amount of BPA at equilibrium (mg/g) for the pseudo-second-order biosorption,  $q_t$  is the amount of biosorbed BPA at time  $t$  (mg/g) and  $k_2$  is the pseudo-second-order kinetic constant rate (g/mg/min). 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 Fig. 4. 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 Barley husk biomass follows the pseudo second order kinetic model.

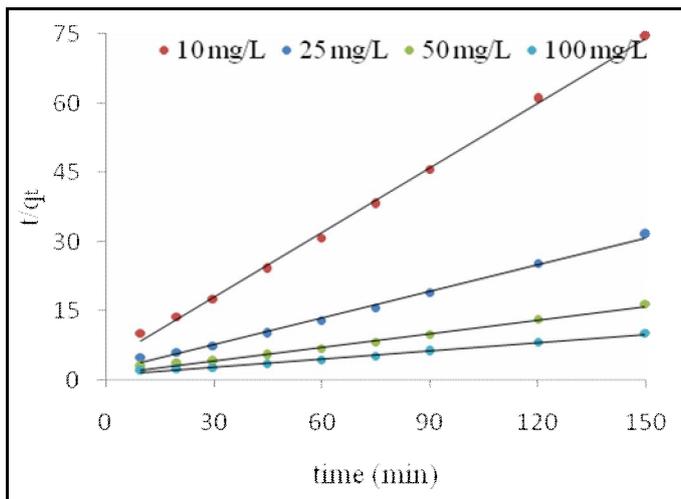
The intraparticle diffusion equation is written as follows(40):

$$q_t = K t^{0.5} + C$$

Where  $C$  is the intercept which describes the foundry layer thickness and  $K$  ( $\text{mg/g min}^{1/2}$ ) is the rate constant of intraparticle diffusion. According to results, values of coefficients of determination from Table 2 are also low.

**Table 2: Kinetic parameters for the adsorption of BPA onto Barley husk at various concentration**

Con (mg/L)	$q_e$ exp	Pseudo-first order			Pseudo-second order			Intra-particle diffusion		
		$K_1$	$q_e$	$R^2$	$K_2$	$q_e$	$R^2$	$K$	$C$	$R^2$
10	1.99	0.445	1.244	0.911	0.044	2.044	0.998	0.144	1.89	0.871
25	4.55	0.596	3.844	0.892	0.065	4.689	0.999	0.225	2.44	0.858
50	9.12	0.873	7.593	0.881	0.081	9.848	0.999	0.411	1.73	0.894
100	16.44	0.959	11.72	0.906	0.098	17.42	0.998	0.652	2.96	0.832



**Fig. 4: Pseudo-second-order kinetic plots for BPA adsorption onto Barley husk**

**Adsorption isotherms:**

The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were used to describe the relationship between the amount of BPA adsorbed and its equilibrium concentration in solutions.

The linear form of Langmuir equation can be written as follows(41):

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

Where  $C_e$  (mg/L) is the concentration of BPA at equilibrium,  $q_e$  (mg/g) is the amount of BPA adsorbed by the barley husk at equilibrium,  $q_m$  (mg/g) is the maximum adsorption capacity corresponding to monolayer coverage, and  $K_L$  (L/mg) is the Langmuir constant.

In order to determine if the dsorption process is favorable or unfavorable, a dimensionless constant separation factor or equilibrium parameter  $R_L$ , is defined according to the following equation(42):

$$R_L = \frac{1}{1 + K_L C_0}$$

Where  $K_L$  (L/mg) is the Langmuir constant and  $C_0$  (mg/L) is the initial BPA concentration.

The linear form of Freundlich equation is given as(24):

$$\text{Log } q_e = \frac{1}{n} \log C_e + \log K_F$$

Where  $q_e$  is the BPA concentration on barley husk at equilibrium,  $C_e$  (mg/L) is the concentration of BPA in solution at equilibrium,  $K_F$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively .

The linear form of Tempkin isotherm can be written as(43):

$$q_e = B \ln(A) + B \ln(C_e)$$

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

The linear form of Dubinin-Radushkevich (D–R) isotherm model can be seen below(44, 45):

$$\ln q_e = \ln q_m - K \varepsilon^2$$

Where  $K$  is a constant corresponding to the biosorption energy,  $q_m$  the theoretical saturation capacity and  $\varepsilon$  is the Polanyi potential which is calculated from equation below(46):

$$\varepsilon = RT \ln(1 + 1/C_e)$$

Where  $R$  ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ ) is the gas constant and  $T$  (K) is the absolute temperature.  $E$  was calculated from the  $K$  value by the following relation(44, 45):

$$E = 1 / (2K)^{1/2}$$

The results of fitting these models are shown in Fig. 5b–d, and the fitting parameters for tetracycline are listed in Table 3. The correlation coefficients were high for Langmuir isotherm and it can be said that the experimental data was fitted better to the Langmuir isotherm model. The Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform adsorption on the surface and no transmigration in the plane of the surface(47). The  $R_L$  value indicates adsorption process is irreversible when  $R_L$  is 0; favorable when  $R_L$  is between 0 and 1; linear when  $R_L$  is 1; and unfavorable when  $R_L$  is greater than 1(38). The value of  $R_L$  was found to be 0.512-0.955 and this again confirmed that the Langmuir isotherm was favorable for adsorption of BPA onto the barley husk biomass under the conditions used in this study. Higher value for  $K_F$  indicates higher affinity for adsorbate and the values of the empirical parameter  $1/n$  lie between  $0 < 1/n < 1$ , indicating favorable adsorption. A similar result was reported for the adsorption of bisphenol on Red mud and *Azolla filiculides*(1, 19).

The mean energy of adsorption is the free energy change when one mole of the ion is transferred to the surface of the solid from infinity in the solution. Its value in the range of 1–8  $\text{kJ mol}^{-1}$  indicates physical adsorption, while its value in the range of 20–40  $\text{kJ mol}^{-1}$  is indicative of the chemisorption(32). The value of  $E$  was found to be 1.573, 2.224 and 2.566 and this again confirmed that the physical adsorption was favorable for adsorption of BPA onto the barley husk biomass under the conditions used in this study.

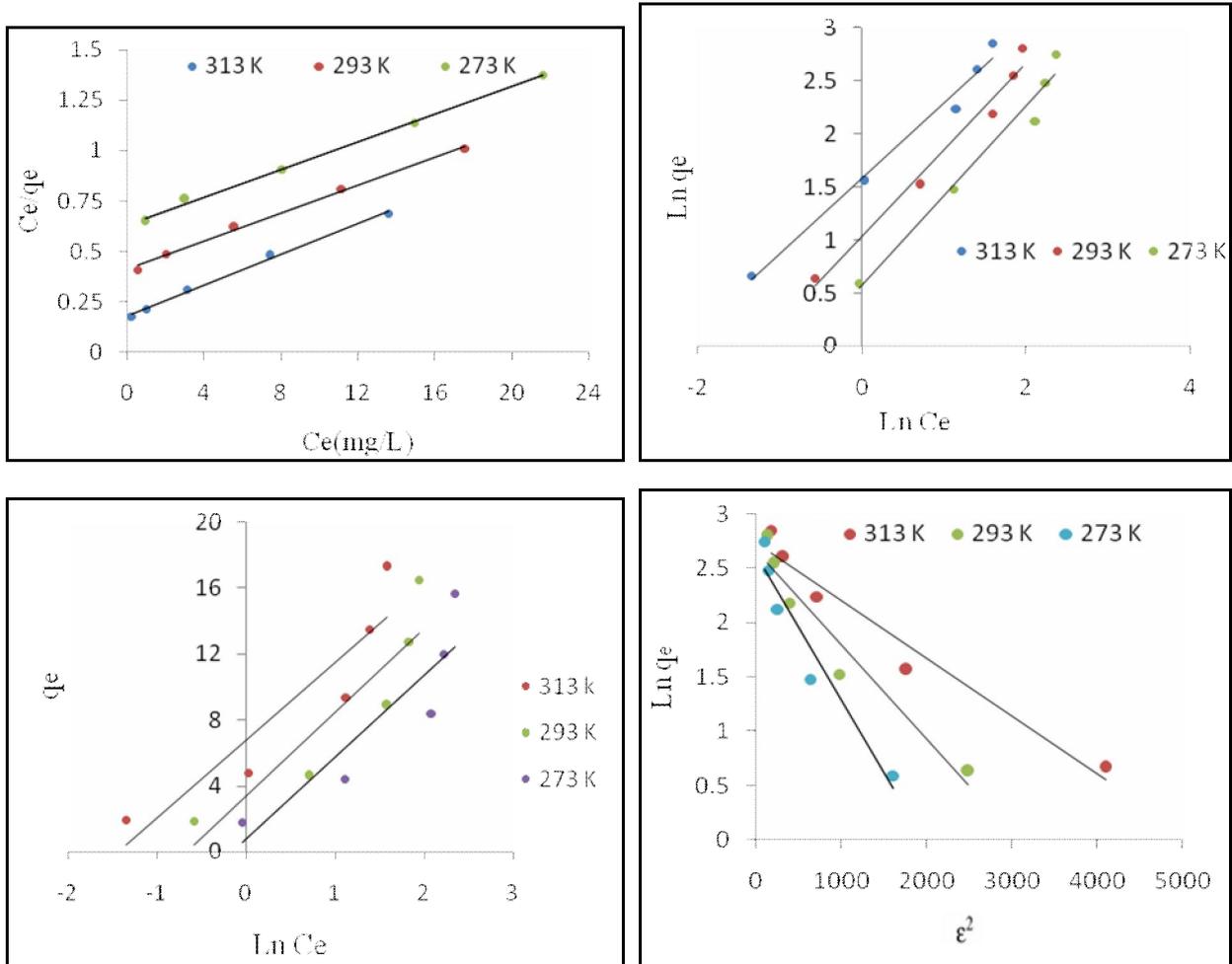


Fig. 5. Adsorption isotherms (a); Langmuir (b); Freundlich (c), Temkin (d) Dubinin-Radushkevich

Table 3: The adsorption isotherms constants for the removal BPA onto Barley husk

Tem (°K)	Langmuir model				Freundlich model			Temkin model			D-Radushkevich		
	qm	RL	KL	R <sup>2</sup>	n	K <sub>F</sub>	R <sup>2</sup>	B	A	R <sup>2</sup>	K	E	R <sup>2</sup>
273	15.51	0.955	0.0028	0.997	2.24	9.45	0.951	26.15	0.884	0.725	0.471	1.753	0.917
293	17.85	0.754	0.0047	0.998	2.95	11.24	0.966	22.31	0.744	0.744	0.319	2.224	0.923
313	19.94	0.512	0.0074	0.999	3.76	13.66	0.972	19.44	0.597	0.688	0.284	2.566	0.936

**Thermodynamic parameters**

Thermodynamic parameters such as standard free energy ( $\Delta G^0$ ) standard enthalpy change ( $\Delta H^0$ ) and standard entropy changes ( $\Delta S^0$ ) were calculated by using equilibrium constant ( $K^0$ ) change with temperature (T). The free energy change can be determined by the following equation(48, 49).

$$\Delta G^0 = -RT \ln K$$

Where  $\Delta G^0$  is the free energy change of sorption process (kJ/mol), K is the equilibrium constant, T is the temperature in (K), R is the universal gas constant. The free energy change may be expressed in terms of enthalpy change of sorption as a function of temperature as follows(50, 51):

$$\Delta G^0 = \Delta H - T\Delta S$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where  $\Delta H^0$  is the standard heat changes of the sorption,  $\Delta S^0$  is the entropy change of sorption (KJ/mol). The standard enthalpy and entropy changes values are evaluated from the slope and intercept of linear plot  $\ln k$  against  $1/T$ . Thermodynamic parameter values for the sorption of BPA on barley husk and the values are tabulated in Table 4. The negative values of free energy changes confirm the spontaneous nature of sorption of BPA on barley husk and the positive values of  $\Delta H^0$  confirm the sorption process of an endothermic nature. The positive values show increased randomness at solid–solution interface during the sorption of BPA on the barley husk.

**Table .4. Thermodynamic Parameters for the Adsorption of BPA**

$C_0$ (mg/L)	$\Delta G^0$			$\Delta H^0$	$\Delta S^0$
	273 K	293 K	313 K		
10	-25.41	-29.72	- 33.83	4.25	48.19
25	-31.22	-37.41	-42.18	5.11	55.64
50	-40.17	-45.56	-51.28	6.35	62.37
100	-49.73	-55.34	-61.15	8.44	67.48

## Conclusion

This study investigated the adsorption of BPA from aqueous solutions onto dried Barley husk biomass. The solution pH played a significant role in influencing the capacity of an adsorbent towards BPA molecules. An increase in the pH of solutions leads to a decrease in the sorption capacities of BPA on the sorbent under study. The sorbed amounts of BPA increase with increase in contact time, reaching a maximum value after 90 min. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of BPA. The pseudo-second-order kinetic model provided the best correlation of the experimental data. The negative value of  $\Delta G^0$  confirms that the feasibility of the reaction and spontaneous nature of the adsorption. The study shows that Barley husk biomass can be effectively used as adsorbent for the removal of BPA from aqueous solutions.

## References

- Zazouli MA, Balarak D, Mahdavi Y, Barafrashtehpour M, Ebrahimi M. Adsorption of Bisphenol from Industrial Wastewater by Modified Red Mud. *Journal of Health & Development*. 2013; 2(1);1-11.
- Yamanaka H, Moriyoshi K, Ohmoto T, Ohe T, Sakai K. Efficient microbial degradation of bisphenol A in the presence of activated carbon. *J Biosci Bioeng*. 2008; 105(2);157-160.
- Zimmers SM, Browne EP, Okeefe PW and Anderton DL. Determination of free Bisphenol A (BPA) concentrations in breast milk of U.S. women using a sensitive LC/MS/MS method. *Chemospher*. 2014; 104; 237–43.
- Brugnera MF, Rajeshwar K, Cardoso JC, Zanoni M, Boldrin V. Bisphenol A removal from wastewater using self-organized TiO<sub>2</sub> nanotubular array electrodes. *Chemosphere*. 2010; 78(5);569-75.
- Saiyood S, Vangnai A.S, Thiravetyan P, Inthorn D. Bisphenol A removal by the *Dracaena* plant and the role of plant-associating bacteria. *Journal of Hazardous Materials*. 2010;178(1-3);777-85.
- Zazouli MA, Mahdavi Y, Bazrafshan E, Balarak D. Phytodegradation potential of bisphenolA from aqueous solution by *Azolla Filiculoides*. *journal Iranian journal of environmental health science and engineering*. 2014;10; 14-20.
- Neamt-u M, Frimme FH. Degradation of endocrine disrupting bisphenol A by 254 nm irradiation in different water matrices and effect on yeast cells. *Water research*. 2006; 40;3745-50.
- Tanaka S, Kuramitz H, Nakata Y, Kawasaki M. Electrochemical Oxidation Of Bisphenol A. Application To The Removal Of Bisphenol A Using a Carbon Fiber Electrode. *Chemosphere*. 2001; 5; 37-43.
- Andrescu S, Ispas CR, Ravalli MT, Steere A. Multifunctional biomagnetic capsules for easy removal of phenol and bisphenol A. *Water research*. 2010;44;1961-9.
- Yoon Y, Flora J.R, Park Y, Heo J, Joseph L. Adsorption of bisphenol A and 17 $\alpha$ -ethinyl estradiol on single walled carbon nanotubes from seawater and brackish water. *Desalination*.2011; 281; 68-74.
- Kang J, Katayama Y, Kondo F. Biodegradation or metabolism of bisphenol A: From microorganisms to mammals. *Toxicology*. 2006; 271;81-90.

12. Dong Y, Wu D, Chen X, Lin Y. Adsorption of bisphenol A from water by surfactant-modified zeolite. *Journal of Colloid and Interface Science*. 2010; 348; 585-90.
13. Joseph J, Heo J, Park Y, Flora J.R, Yoon Y. Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments. *Desalination*. 2011; 281;68–74.
14. Loffredo E, Traversa A, Senesi N. Biodecontamination of water from bisphenol A using ligninolytic fungi and the modulation role of humic acids. *Ecotoxicol Environ Saf*. 2012; 79;288–293.
15. Liu G, Ma J, Li B, Qin Q. Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments. *Hazard Mater*. 2009; 164;1275–1280.
16. Zhang Y, Causserand C, Aimar P, Cravedic J. Removal of bisphenol A by a nanofiltration membrane in view of drinking water production. *Water research*. 2006; 40:3793-9.
17. Sajiki J, Yonekubo J. Inhibition of seawater on bisphenol A (BPA) degradation by Fenton reagents. *Environ Int*. 2004;30:145–150.
18. Diyanati RA, Yazdani J, Belarak D. Effect of sorbitol on phenol removal rate by lemna minor. *Mazandaran university of medical science*. 2013;22(2):58-64.
19. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. The ability of Azolla and lemna minor biomass for adsorption of phenol from aqueous solutions. *J Mazandaran University Medical Science*. 2013, 23(106);21-8.
20. Gulbeyi D, Cicek H, Dursun AY. Adsorption of phenol from aqueous solution by using carbonised beet pulp. *Journal of Hazardous Materials*.2013;125(1-3);175-82.
21. Ihaddadene B, Tifouti L, Al-Dujaili AH, Gherraf N. Enhancing Batch Adsorption capacity of Bentonite, Kaolinite and their Organomodified Forms for Phenol removal. *International Journal of ChemTech Research*. 2015;8(4); 1749-1762.
22. Sui Q, Huang J, Liu Y, Chang X, Ji G, Deng S. Rapid removal of bisphenol A on highly ordered mesoporous carbon. *Journal of Environmental Sciences*. 2008; 23(2);172-82.
23. Tsai W, Lai C, Su T. Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorbents. *J Hazard Mater*. 2006; 134;169-175.
24. Daniel S, Syed shabudeen PS. Acid dye removal by using modified activated carbon encapsulated with nano particles. *International Journal of ChemTech Research*. 2015;8(2); 845-85.
25. Zazouli MA, Mahvi AH, Mahdavi Y, Balarak D. Isothermic and kinetic modeling of fluoride removal from water by means of the natural biosorbents sorghum and canola. *Fluoride*. 2015;48(1):15-22.
26. Dina, M. Bhattia, HN. Yasira, M. Ashrafa, A. Direct dye biosorption by immobilized barley husk. *Desalination and Water Treatment*. 2015; 54;45-53.
27. Maleki A. Mahvi AH. Zazouli MA. Izanloo H. Barat AH. Aqueous Cadmium Removal by Adsorption on Barley Hull and Barley Hull Ash. *Asian Journal of Chemistry*. 2011; 23(3);1373-1376.
28. Haq I, Bhatti HN, Asgher M. Removal of solar red BA textile dye from aqueous solution by low cost barley husk: Equilibrium, kinetic and thermodynamic study. *Canadian Journal of Chemical Engineering*. 2011; 89(3);593–600.
29. Robinson T. Chandran B. Nigam P. Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. *Environment International*. 2002; 28(1-2);29–33.
30. Robinson T. Chandran B. Nigam P. Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption. *Bioresource Technology*. 2002; 85(2);119–124.
31. Swapna Sundari D, Kariman A, Mansouri HR, Kariman F. The Effectiveness of natural, Low Cost Adsorbent for Removal of Methylene Blue. *International Journal of ChemTech Research*. 2014;7(6);2763-2768.
32. Zazouli MA, Belarak D, Karimzadeh F, Khosravi F. Removal of Fluoride from Aqueous Solution by Using of Adsorption onto Modified Lemna Minor: Adsorption Isotherm and Kinetics Study. *J Mazandaran University Medical Science*. 2014;24(109):41-8.
33. Zazouli MA, Yazdani J, Balarak D, Ebrahimi M, Mahdavi Y. Removal Acid Blue 113 from Aqueous Solution by Canola. *J Mazandaran University Medical Science*. 2013; 23(2);73-81.
34. Dursun AY, Kalayci CS. Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin. *Journal of Hazardous Materials*. 2005;123;151–7.
35. Palanisamy PN, Agalya A, Sivakumar P. Equilibrium Uptake and Sorption Dynamics for the Removal of Acid Dyes Using Euphorbia tirucalli Wood. *International Journal of ChemTech Research*. 2014; 6(2);1478-1488.
36. Diyanati RA, Yousefi Z, Cherati JY, Balarak D. Adsorption of phenol by modified azolla from Aqueous Solution. *Journal of Mazandaran University of Medical Science*. 2013; 22(2);13-21.

37. Shrivastava VS. Removal of Congo red dye from aqueous solution by *Leucaena leucocephala* (Subabul) seed pods. *International Journal of ChemTech Research*. 2014; 6(2); 1038-1043.
38. Shelke R, Bharad J, Madje B, Milind, Ubale M. Adsorption of acid dyes from aqueous solution onto the surface of acid activated Nirgudi Leaf powder (AANLP): A case study. *International Journal of ChemTech Research*. 2010; 2(4); 2046-2051.
39. Saja S. Al-Taweel. Equilibrium Isotherm and Kinetic Studies of Adsorption of Basic Green-4 on Titanium Dioxide Nanoparticles. *International Journal of ChemTech Research*. 2015;8(10);116-125.
40. Choudhary P, Singh J and Subramanian S. Biosorption of acidic dye from an aqueous solution by a marine bacterium, *Planococcus* sp. *International Journal of ChemTech Research*. 2015;8(4); 1763-1768.
41. Chandra S. *Elephas Maximus* Dung Activated Carbon as a Biosorbent for Methylene Blue Removal: Equilibrium and Kinetic Studies. *International Journal of ChemTech Research*. 2014;6(5); 1593-1599.
42. Balarak D, Jaafari J, Hassani G, Mahdavi Y, Tyagi I, Agarwal S, Gupta VK. The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies. *Colloids and Interface Science Communications*. 2015; 7;16-19.
43. Senthilkumar G, Murugappan A. Kinetic Modeling and Multicomponent Isotherm Studies on Adsorption of Multi Heavy Metal Ions in MSW Leachate by Alcoffine. *International Journal of ChemTech Research*. 2015;8(6);324-343.
44. Khatod I. Removal Of Methylene Blue Dye From Aqueous Solutions By Neem Leaf And Orange Peel Powder. *International Journal of ChemTech Research*. 2013; 5(2);572-577
45. Jirekar DB, Pramila G, Mazahar Farooqui M. Kinetics and Isotherm Studies on Crystal Violet Dye Adsorption onto Black Gram Seed Husk. *International Journal of ChemTech Research*. 2014;7(1); 427-43.
46. Basker A, Syed shabudeen PS, Vignesh kumar P. Evaluation of Adsorption Potential of the Agricultural Waste Areca Husk Carbon for Methylene Blue. *International Journal of ChemTech Research*. 2014; 6(2);1309-1324.
47. Tamilselvi S, Asaithambi M. Microwave Assisted Synthesis of Activated Carbon Fibers from Silk Cotton. *International Journal of ChemTech Research*. 2015;7(1);375-381.
48. Manivannan P, Arivoli S, Mohammed R. Equilibrium and Thermodynamics Studies on the Removal of Iron (III) onto Activated Hibiscus Sabdariffa Stem Nano Carbon. *International Journal of ChemTech Research*. 2015;8(10);346-354
49. Jayasanthakumari H, Krishnamoorthy P, Arumugam TK. Removal of Rhodamine B from aqueous solution by activated carbon prepared from the natural plant *Typha latifolia* by adsorption: Kinetic and Isotherm Studies. *International Journal of ChemTech Research*. 2015;7(7);2867-2874.
50. Zazouli MA, Mahvi AH, Dobaradaran S, Barafrahshtehpour M, Mahdavi Y, Balarak D. Adsorption of fluoride from aqueous solution by modified *Azolla Filiculoides*. *Fluoride*. 2014;47(4);349-58.
51. Balarak D, Mahdavi Y, Bazrafshan E, Mahvi AH, Esfandyari Y. Adsorption of fluoride from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetic and thermodynamic parameters. *Fluoride*. 2016;49(1);35-42.
52. T.K.Manimekalai, G.Tamilarasan, N.Sivakumar & S.Periyasamy; Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using plastic waste activated carbon prepared by CO<sub>2</sub> activation; *International Journal of ChemTech Research*; 2015, Vol.8, No.6, pp 225-240.
53. Saja S. Al-Taweel; Equilibrium Isotherm and Kinetic Studies of Adsorption of Basic Green-4 on Titanium Dioxide Nanoparticles; *International Journal of ChemTech Research*; *International Journal of ChemTech Research*; 2015, Vol.8, No.10 pp 116-125.
54. A.Geetha\* and P.N.Palanisamy; Kinetics and Equilibrium Studies on The Removal of Anionic Dyes using Polyaniline Coated Sawdust Composite; *International Journal of ChemTech Research*; 2015, Vol.7, No.5, pp 2439-2447.

\*\*\*\*\*