



Adsorptive removal of Bisphenol A from aqueous solutions by *Pistacia atlantica*: isotherm and kinetic Studies

Shahin Ahmadi^{1*}, Ferdous Kord Mostafapoor²

^{1*} Dept. of Environmental Health, School of Public Health, Zabol University of Medical Sciences, Zabol, Iran

²Dept. of Environmental Health, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran

Abstract The aim of this study is to investigate the possibility of *Pistacia atlantica* Biomass as an alternative adsorbent for Bisphenol A (BPA) removal from aqueous solution. The effect of various parameters including contact time, solution pH, adsorbent dosage and Bisphenol A concentration was investigated in this experimental-lab study. Also, the isotherm and kinetic studies was performed for phenol adsorption process. The adsorption equilibriums were analyzed by Langmuir, Temkin, Freundlich and Harkins Jura isotherm models. It was found that the data fitted to Langmuir ($R^2=98$) better than other isotherm models. Batch kinetic experiments showed that the adsorption followed Pseudo second -order kinetic model with correlation coefficients greater than 0.99. According to achieved results, it was defined that *P. atlantica* not only was an inexpensive adsorbent, but also a quite effective factor in removal of BAP water and wastewater.

Keywords Adsorption, Aqueous solution, *Pistacia atlantica*, Bisphenol A

Introduction

Among Organic compounds, Bisphenol A is very hazardous compound to humans and environment. Bisphenol A its derivatives are used as intermediates for the manufacturing of various synthetic compounds such epoxy resins, plastics and paints [1-2]. Bisphenol A is considered as priority pollutants since they are harmful to organisms at low concentrations [3-4]. Thus, there is fully recommended to remove the Bisphenol A from industrial effluents before entering the water stream [5]. Several treatments methods for the removal of Bisphenol A from contaminated waters, including oxidation, biodegradation, chemical coagulation, solvent extraction, incineration, reverse osmosis and adsorption and other processes, among which adsorption is one of the most effective techniques in either laboratory or industrial scale [6-8]. Recently, physicochemical methods have been used for removal organic material in wastewaters. Consequently, amongst numerous techniques, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment because of their proven efficiency in the removal of organic and mineral pollutants and for economic considerations [9]. The adsorption method using active carbon was not cost effective because of high operating costs. Many low-cost adsorbents have been studied on BAP removal, such as novel adsorbent rice husk, corncobs, bamboo, saw dust, activated carbon, [10-12], coal fly ash and clays [13], are normally used. *Pistacia atlantica* is a species of pistachio tree known by the English common name Mt. Atlas mastic tree and as the Persian turpentine tree. In Iran it is called Baneh [14]. Three *Pistacia* species naturally occur in Iran: *P. Vera* L., *P. khinjuk* Stocks and *P. atlantica* Desf. *P. atlantica* has three subspecies or varieties which have been described as *cabulica*, *kurdica*, and *mutica* (15). *Pistacia atlantica* was studied as it is a fast growing plant in East of Iran [15-16]. *P. atlantica* because of its high absorption properties has many applications in several countries to remove the organic material such as Aniline (16).



The adsorption of Bisphenol A has been investigated as a function of contact time, pH, BAP concentration and adsorbent dose. In this research, the *Pistacia atlantica* shells were applied for the adsorption of Bisphenol A (BAP) from aqueous solutions as adsorbent.

Materials and Methods

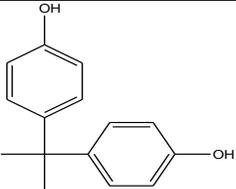
Preparation of adsorbent

Pistacia atlantica was collected from zahedan city, Iran. It was washed thoroughly with distilled water, dried at 105 °C for 24 hours. The each 10 gr of *Pistacia atlantica* was activated by using of 20 ml sulphuric acid for 24 h. Then, it was rinsed 3 times by the distilled water. It was dried in 110 °C for 1 h. After that the *P. atlantica* was grinded and sieving by using a 100 mesh sieve (16).

The characteristics of BAP

The used Bisphenol A was the analytical grade which was purchased from Sigma Aldrich Co, Germany. The stock solution (1000mg/L) was prepared and desired concentration of Bisphenol A solution was prepared by dilution of stock solution. General characteristics and chemical structures of BPA are presented in Table1.

Table 1: Characteristics of BPA

Names	Molecular Weight	λ_{\max} (nm)	Molecular formula	Structure
P,p'-isopropylidenebis phenol	228.1g/mol	276	C ₆ H ₅ ClO	
2,2-bis(4-hydroxyphenyl)propane				

Batch adsorption experiments : The batch adsorption system was employed in present study and the most effective factors for adsorption process including contact time (10-115 min), pH (2,4,6,8), adsorbent dose (4-15 g L⁻¹) and initial concentration of BPA (50- 150 mg L⁻¹) were assessed. The optimum pH was determined by varying the pH in range of 2-8 and keeping constant of other variables (contact time, adsorbent dose and initial BPA concentration). The experiments were performed in 100 milliliter beaker with a constant concentration of BPA. Then this mixture was shaken with a shaker device of enforce model with 150 rpm and the room temperature of 20 – 25°C. HCl and NaOH were used to adjust the pH solution. In the next step, the optimum adsorbent dose was estimated by keeping constant of contact time and initial BPA concentration and also the obtained optimum pH. After determination of the optimum pH and adsorbent dose, the various concentrations of the BPA in the specified times of contact was investigated. The final BPA concentration in solution was measured by the UV-Visible spectrophotometer at a wavelength 276nm (16, 17).

The removal efficiency and sorption capacity of the *P. atlantica* were determined by Eq. (1) and (2), respectively (24):

$$R = \left[\frac{C_0 - C_f}{C_0} \right] \times 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

Where; R (%) and q_e (mg/g) are the removal efficiency and adsorption capacity, respectively. C₀ (mg /L) and C_f are the initial and final concentration, C_e (mg/ L) is concentration at the equilibrium, m (g) is the mass of the adsorbent and V (L) is the volume of the solution.

Results and Discussion

Effect of pH and initial aniline concentration

The pH value of the solution was an important controlling parameter in the adsorption process, as can be seen from Fig. 1. The effect of pH on BPA uptake in the batch process was studied by varying the pH from 2 to 8. It shows



that On the basis of the maximum removals of BPA for contact time 10 min were carried out at pH 4. As shown in Fig. 1, the removal percent 82% at biosorbent dosage from 6 g/L.

BPA is a weak acid compound and pKa value for BPA is 9.5; so at pH high than 9.5 have a negatively charged. In this situation, efficiency is reduced due to electrostatic disposal. In addition, at acid pH, the adsorption of BAP increases because phenol was undissociated and the dispersion interaction predominated (18).

To determine the effect of initial BPA concentration on the adsorption process the initial concentration of BPA was varied from 50 to 150 mg/L at the fixed pH 4, adsorbent dose 6 g/L and contact time 10 min. As presented in figure 2, BAP removal efficiency decreased with increasing of BPA concentration, so maximum efficiency was achieved at initial BPA concentration 50 mg/L while the q_e increased from 50 to 150 mg/g. This may be due to the limited number of active sites on the adsorbent that becomes saturated at high concentration of BPA. In other words, at low concentrations, the availability of BPA molecules to adsorption sites is more than high concentrations [19].

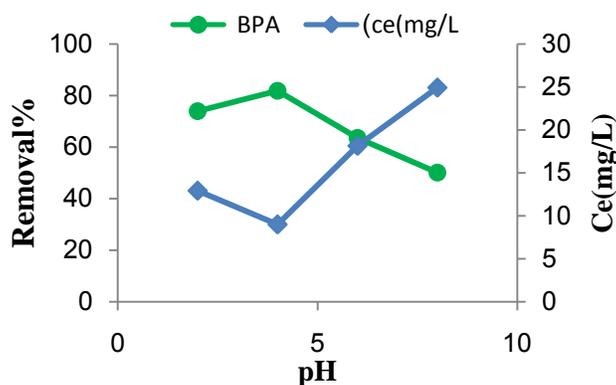


Figure 1: Effect of pH on removal efficiency of BPA
(Contact time =10 min, dosage: 6g/L, initial concentration: 50 mg/L)

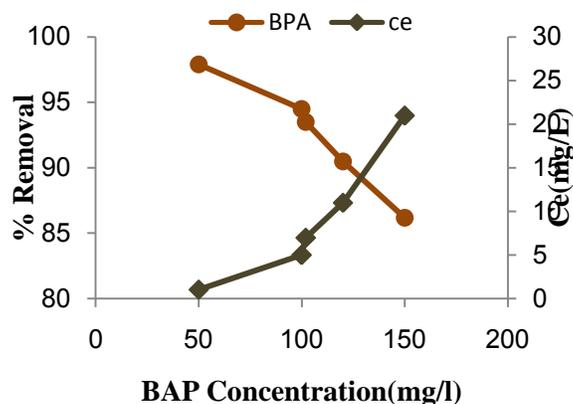


Figure 2: Effect of BAP concentration on removal efficiency of BAP
(Time = 10 min, dosage: 6g/l, pH =4)

Effect of adsorbent dose and contact time

The percentage of BAP removal steeply increases with the adsorbent loading up to 10 g/L, but C_e adsorbed decreased as the dose of adsorbent increases from 4 to 10 g/L.

The adsorption rate decreased by increasing of adsorbent dose 10 to 15 g/L which it is due to the limited number of active sites on the adsorbent and decreasing of the active surface of adsorbent [20].

The contact time between adsorbate and adsorbent is one of the most important design parameters that affect the performance of adsorption processes. Figure 4 shows the effect of contact time on the percent removal efficiency of BAP onto the *P. atlantica* at a constant initial BAP concentration (50 mg/L) and optimum adsorbent dosage and pH.



The uptake of BAP on *P. atlantica* was rapidly in the first 45min then the adsorption rate and finally reached equilibrium in about 60 min. The optimum contact time was 45min which it can probably describe by greater contact surface of *P. atlantica* adsorbent because the increasing of specific surface area can lead to more adsorption percentage in lower time [16, 21].

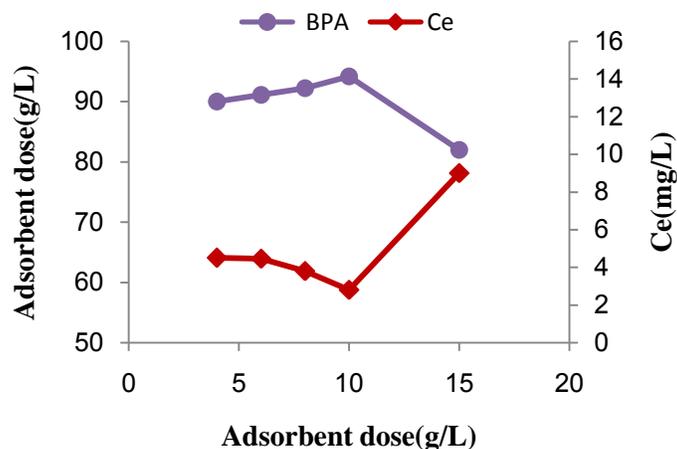


Figure 3: Effect of adsorbent dose on removal efficiency of BAP (Contact time = 10 min, pH 4, BAP concentration: 50 ppm)

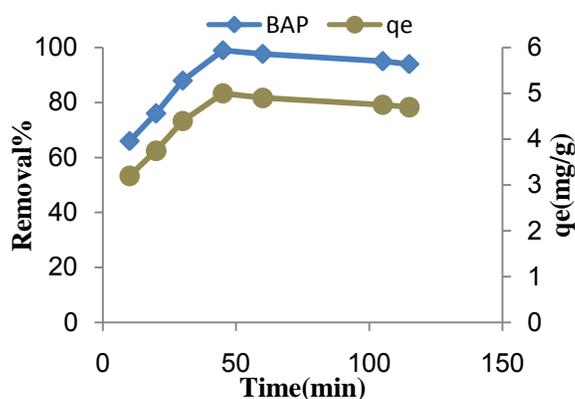


Figure 4: Effect of contact time on removal efficiency of BAP (pH, dosage and concentration: optimum)

Adsorption Isotherms

The equilibrium adsorption isotherm is importance in the design of adsorption systems. Although several isotherm equations are available, but four important isotherms including Langmuir, Harkins Jura and Freundlich isotherms were selected. The Isotherms equations are presented the Table 2.

Table 2: The equation of isotherms [16-17]

Model	Equation
Langmuir	$\frac{c_e}{q_e} = \frac{1}{q_m k_l} + \frac{c_e}{q_m} \quad (3)$
Freundlich	$\text{Log } q_e = \frac{1}{n} \text{log } c_e + \text{log } k_f \quad (4)$
Harkins Jura	$\frac{1}{q_e^2} = \left[\frac{B_{HJ}}{A_{HJ}} \right] - \left[\frac{1}{A_{HJ}} \right] \text{log } C_e \quad (5)$



The Langmuir isotherm is presented the Eq. 3 .Where q_e is the amount of sorbate adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the sorbate or the sorbate unadsorbed in the solution (mg/L); q_m (mg/g) is the maximum theoretical biosorption capacity and K_L (L/mg) is a measure of adsorption energy that is indicated on the affinity between biosorbent and sorbate. The essential features of Langmuir can be expressed in terms of dimensionless constant separation factor R_L which is calculated using the following equation (6):

$$R_L = \frac{1}{1+K_L C_0} \quad (6)$$

Values of R_L indicate the shapes of isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$).

The Freundlich equation is given by Eq 4 .Where q_e is the sorbate adsorbed at the equilibrium (mg/g); C_e is the equilibrium concentration of the sorbate or the unadsorbed sorbate in the solution (mg/L); K_F is a constant, indicative of biosorption capacity.

The Harkins Jura [22] accounts for multilayer adsorption and supports heterogeneous pore distribution. Eq 5.The values of constants B and A were obtained from linear plot of $1/q_e^2$ and $\log C_e$ at 30 °C. The values of constants A and B along with regression coefficient are listed in Table 3. A_{HJ} is Harkins-Jura isotherm parameter which accounts for multilayer adsorption and explains the existence of heterogeneous pore distribution, while B_{HJ} is the isotherm constants [22,-23]. The results and correlation coefficients for isotherms model are presented in Table 3 and fig 5. The results showed that phenol on dried *P. atlantica* fitted according to Langmuir Model isotherm model ($R^2=0.98$). Freundlich ($R^2=0.97$) better than Harkins Jura model ($R^2=0.94$).

Table 3: The adsorption isotherms constants for the removal aniline and phenol

Langmuir				Freundlich			Harkins Jura		
q_m	R_L	K_L	R^2	n	K_F	R^2	B_{HJ}	A_{HJ}	R^2
8	0.006	3	0.98	2.8	8.18	0.97	1.5	159	0.94

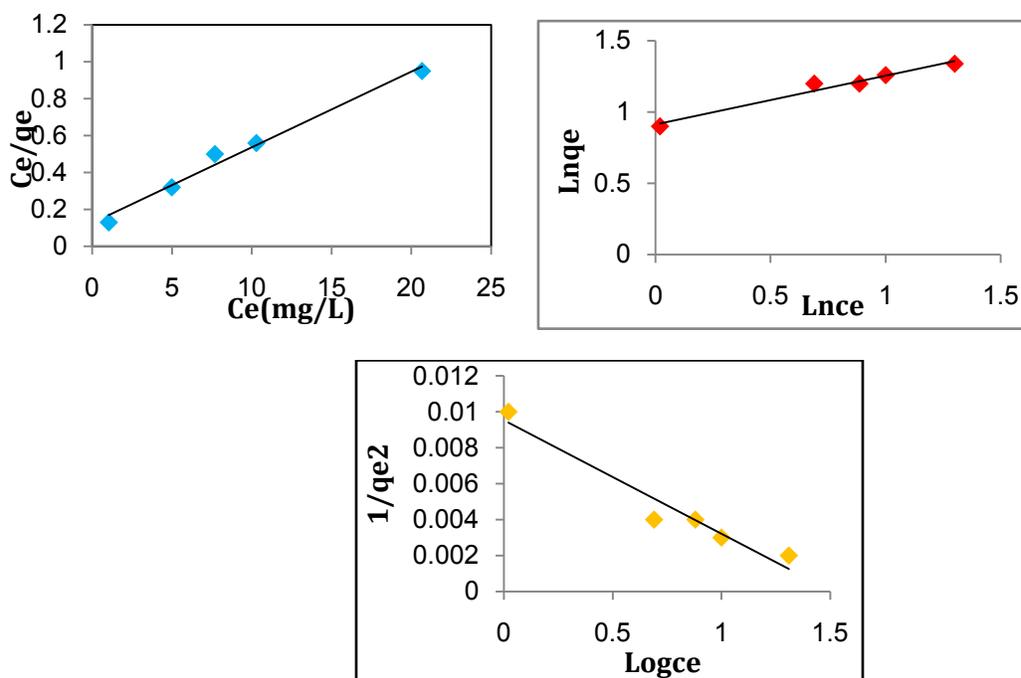


Figure 5: Adsorption isotherms (a); Langmuir (b); Freundlich (c), Harkins Jura



Adsorption Kinetics

Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. The study of kinetic models was performed in contact time between 10-115 min with aniline and phenol concentration of 50 mg/l and optimum amount of pH and adsorbent dose. To evaluate the differences in the biosorption rates and uptakes, the kinetic data were described with pseudo first and pseudo second order models. The linearized form of model is shown in Table 4.

Table 4: The equation of kinetics [22]

Model	Equation
pseudo-first-order	$\text{Log}(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$ (7)
pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2q^2} + \frac{t}{q_e}$ (8)

Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. In present work, obtained kinetic data from batch studies have been analyzed by using the pseudo second-order and pseudo first order model. The pseudo-first-order rate equation is expressed as Eq. 7 [24-25].

Where q_e and q are the amounts of phenol adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of adsorption (min^{-1}). Values of k_1 were calculated from the plots of $\log(q_e - q)$ versus (t) for different concentrations. Also the pseudo-second-order rate equation has been given by equation 8 [16, 26]. And Where K_2 the second order rate constant ($\text{g mg}^{-1}\text{min}^{-1}$), q and q_e are the amount of the adsorbed on the adsorbent (mg/g) at equilibrium and at time t (min).

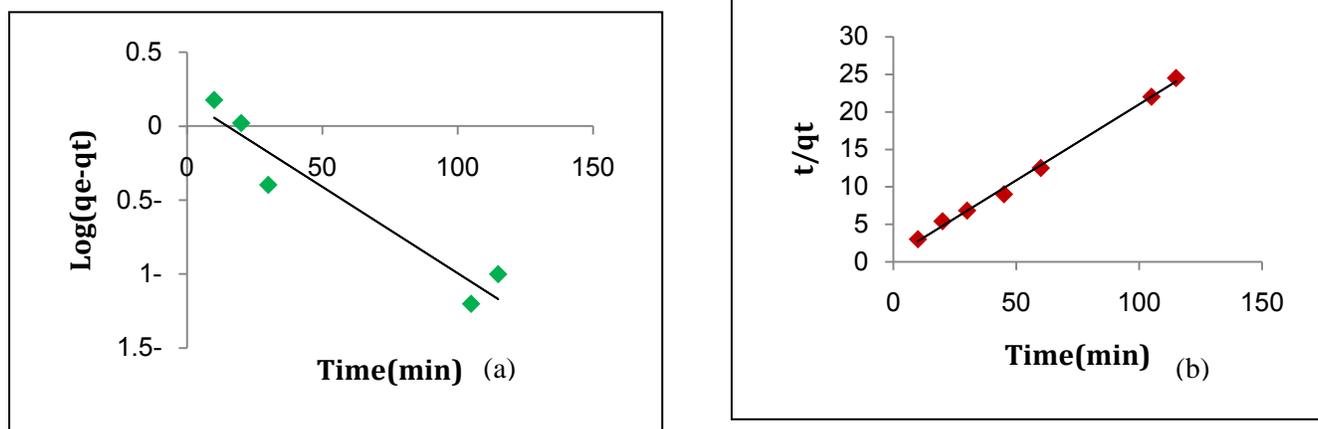


Figure 6: Kinetic isotherms (a); pseudo first order (b); pseudo-second-order

The results and correlation coefficients for Kinetic model are presented in Table 5. By comparing the correlation coefficients R^2 , it can be seen that the experimental equilibrium sorption data are better described by the pseudo second-order model than by the other models.

Table 5: The adsorption kinetic model constants for the removal aniline and phenol

$C_0(\text{mg/l})$	Pseudo second-order			Pseudo First-order		
	$K_2(\text{g/mg min})$	$Q_e(\text{mg/g})$	R^2	$K_{1(1/\text{min})}$	$Q_e(\text{mg/g})$	R^2
BAP	0.055	4.93	0.996	0.398	1.5	0.919

The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant which means the uptake process follows the pseudo-second-order expression with correlation coefficients was always greater of 0.996. The correlation coefficient in pseudo second-order model was better than the first order model correlation coefficients and similar results are shown using removal organic compounds on another adsorbent [27].



Conclusion

This study investigated the adsorption of Bisphenol A from aqueous solutions onto dried *P. atlantica* biomass. The solution pH played a significant role in influencing the capacity of an adsorbent towards phenol molecules. An increase in the pH of solutions leads to a decrease in the sorption capacities of BAP on the sorbent under study. The sorbed amounts of BAP increase with increase in contact time, reaching a maximum value after 45 min. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of Bisphenol A. The pseudo-second-order kinetic model provided the best correlation of the experimental data. The study shows that *P. atlantica* biomass can be effectively used as adsorbent for the removal of Bisphenol A from aqueous solutions.

References

1. Scheck CK, Frimmel FH. Degradation of phenol and salicylic acid by ultraviolet radiation/hydrogen peroxide/oxygen. *Water Research*. 1995; 29(10); 2346-52.
2. An F, Feng X, Gao B. Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO₂. *Chemical Engineering Journal*. 2009 ; 151(1);183-7.
3. N. Calace, E. Nardi, B.M. Petronio, M. Pietroletti, Adsorption of phenols by papermillsludges, *Environ. Pollut.* 2002;118 ; 315–319.
4. F. Akbal, A.N. Onar, Photo catalytic degradation of phenol, *Environ. Monit. Assess.*2003; 83 ; 295–302.
5. B. Ozkaya, Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models, *J. Hazard. Mater.*2006; 129; 158–163.
6. Goncharuk VV, Kucheruk DD, Kochkodan VM, Badekha VP. Removal of organic substances from aqueous solutions by reagent enhanced reverse osmosis. *Desalination*. 2002; 143(1); 45-51.
7. Rodrigues LA, da Silva ML, Alvarez-Mendes MO, dos Reis Coutinho A, Thim GP. Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds. *Chemical Engineering Journal*. 2011;174(1);49-57
8. B. Pan, B. Pan, W. Zhang, Q. Zhang, Q. Zhang, S. Zheng, Adsorptive removal of phenol from aqueous phase by using a porous acrylic ester polymer, *J. Hazard. Mater.*2008; 157 ; 293–299.
9. Deng, H., Li ,G., Yang, H., J. Tang, J. Preparation of activated carbons from cotton stalk by microwave assisted KOH and K₂CO₃ activation. *Chem. Eng. J.*2010; 163; 373–381
10. Tilaki RA. Effect of glucose and lactose on uptake of phenol by lemnamior. *Environmental health*. 2010;7(2):123-8.
11. S.W. Won, H. Kim, S. Choi, B. Chung, K. Kim, Y. Yun, Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent, *Chem. Eng. J.*2006; 121 ; 37–43.
12. F. Batzias, D. Sidiras, E. Schroederb, C. Weber, Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems, *Chem. Eng. J.* 2009;148;459–472.
13. M. Ahmedna, W.E. Marshall, R.M. Rao, Production of granular activated carbons from selected agricultural by-products and evaluation of their physical,chemical and adsorption properties, *Bioresour. Technol.*2000; 71 ; 113–123.
14. Pourreza M. Sustainability of wild pistachio (*Pistacia atlantica* Desf.) in Zagros forests, Iran. *Forest Ecology and Management*.2008; 255 3667-71
15. Razavi S. Pistachio production, Iran vs. the World. *Acta Horti.*2006; 726,689–694.
16. Ahmadi Sh, Mostafapoor F. Adsorptive removal of aniline from aqueous solutions by *Pistacia 4 atlantica* (Baneh) shells: isotherm and kinetic studies. *J. Sci. Technol. Environ. Inform.*2017; 4(2):313-326.DOI:10.18801/jstei.040217.34.
17. Deng H, Li G, Yang H, J. Tang, J. Preparation of activated carbons from cotton stalk by microwave assisted KOH and K₂CO₃ activation. *Chem. Eng. J.* 2010;163; 373–381.



18. Zhang Y, Causserand C, Aimarb P, Cravedic J. Removal of bisphenol A by a nanofiltration membrane in view of drinking water production. *Water research*. 2006; 40:3793-9.
19. Taherkhani F., Leili, M., Tarlani Azar, M.& Faradmal,J.The Optimization of Aniline Adsorption from Aqueous Solutions by Raw Bentonite and Bentonite Modified with Cationic Surfactants Using the Taguchi Model.2015; 22(1), 55-64.
20. Kim, SH., Shon, HK.& Ngo, HH. Adsorption characteristics of antibiotics trimethoprim on powdered and granular activated carbon. *J. Ind. Eng. Chem*2010; 16, 344-349.
21. 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.
22. Ibrahim, M. B., Sani, S. Comparative Isotherms Studies on Adsorptive Removal of Congo red from Wastewater by Watermelon Rinds and Neem-Tree Leaves *Open Journal of Physical Chemistry*.2014; 4, 139-146.
23. Suyamboo, B.K., Perumal, R.S.Equilibrium, Thermodynamic and Kinetic Studies on Adsorption of a Basic Dye by *Catullus lanatus* Rind. *Iranian Journal of Energy & Environment*2010; 3, 23-34
24. Sui Q, Huang J., Liu Y., Chang, X., Ji, G.&Deng ,S. Rapid removal of biphenyl A on highly ordered Mesoporous carbon. *Journal of Environmental Sciences*,2008;23(2),172-82.
25. Ali I. Water treatment by adsorption columns: Evaluation at ground level. *Sepn.& Purfn. Rev.*2014; 43,175-2015.
26. Mahvi, A. & Heibati, B. Removal efficiency of azo dyes from textile effluent using activated carbon made from walnut wood and determination of isotherms of acid red18. *Public Ardabil*2009; 1(3),7-15.
27. Radhika, M.& Palanivelu, K. Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent: Kinetics and isotherm analysis. *J. Hazard Mater.*2006;138,116–119

