Original Article

Adsorption Isotherm and Kinetics Study: Removal of Phenol Using Adsorption onto Modified Pistacia mutica shells

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(Received: 23 Jul. 2017; Revised: 12 Nov. 2017; Accepted: 27 Dec. 2017)

Abstract

Background and purpose: Phenol is an aromatic hydrocarbon and one of the banzan derivatives which has a higher dissolution rate in water. Therefore, it must be removed for water pollution prevention. The aim of this study was to investigate the possibility of Pistaciamuticabio mass as an alternative adsorbent for phenol removal from aqueous solution.

Materials and Methods: The effect of various parameters including contact time (10-102 min), pH(2-8), adsorbent dosage (0.4-1.5g/L), phenol concentration (50-150mg/L) were investigated in this experimental-lab study. Also, the isotherm and kinetic investigations were performed for phenol adsorption process. The adsorption equilibriums were analyzed by Langmuir, Temkin, Freundlich and Harkins Jura isotherm models.

Results: It was found that the data fitted to Langmuir (R^2=0.98) better than other isotherm models. Batch kinetic experiments showed that the adsorption followed Pseudo second-order kinetic model with correlation coefficients greater than 0.998.

Conclusion: It was revealed that P. mutica was not only an inexpensive absorbent, but also a quite effective factor in removal of phenol from water and wastewater.

Keywords: Adsorption; Aqueous solution; Pistacia mutica; phenol

Citation: Sarvani R, Damani E, Ahmadi Sh. Adsorption Isotherm and Kinetics Study: Removal of Phenol Using Adsorption onto Modified Pistacia mutica shells 2018; 6 (1):33-42

1. Introduction

Phenol and its derivatives are used as intermediates for the manufacturing of various synthetic compounds, such as dye stuffs, rubbers, pesticides, plastics, and paints (1-2). Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations (3, 4) due to their toxicity and carcinogenicity properties. The US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/L (5). Thus, it is fully recommended to remove the phenol from industrial effluents before entering the water stream (6).Several treatments methods for the removal of phenol 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 (7, 8, 9). 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 (10). The previous studies have indicated that the adsorption onto activated carbon was a reliable, inexpensive and significantly effective technique to remove the phenol; however, the high cost of activated carbon limits the use of activated carbon (11). Many low-cost adsorbents have been investigated on phenol removal, such as lemnaminor (12), coconut shell, rice husk, corncobs, bamboo, saw dust, activated carbon, (13, 14), coal fly ash, and clays (15), which are normally used. This pistacia mutica is the most economically important tree in many parts of Iran including the Zagros Mountains, where it is managed as a valuable forest tree (15, 16). Pistacia mutica is the most economically important species for rural people in areas of natural forest (16). The fruit of p. mutica is also an important source of food, although the fruits are smaller and not as commercially valuable as those produced in orchards (primarily from cultivars of Pistacia Vera L). Old trees may have trunks measuring 2 m (6 ft 7 in) in diameter; it may take 200 years for a tree to reach 1 m wide (17,18). The main purpose of this study was to investigate the P.mutica shells efficiency in the removal of phenol from aqueous solution. The impact of various factors such as the contact time, adsorbent dosage, pH and initial concentration of phenol were studied to determine the optimal conditions. Finally, the adsorption isotherm and kinetic models have been studied.

2. Materials and methods:

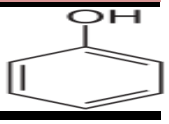
2.1. Preparation of adsorbent

Pistacia mutica was collected from Zahedan city, Iran. It was washed thoroughly with distilled water, dried at 105^{o}C for 24 hours. Each 10 gr of P.mutica was activated by using 20 ml of sulphuric acid for 24 h. Then, it was rinsed 3 times by distilled water. Next, it was dried in 110^{o}C for 1 h. After that the P.mutica was grinded and sieved by using a 100 mesh sieve (19).

2.2.The characteristics of phenol

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

Table1. Characteristics of phenol (9)

Name	Molecular weight	λ_{max}(nm)	Molecular formula	Structure
phenol	94.11g/mol	**500nm**	C_6H_5OH	

2.3.Batch adsorption experiments

The batch adsorption system was employed in the present study, and the most effective factors for adsorption process including contact time (10-105 min), pH (2,4,6,8), adsorbent dose (0.4-1.5 g L^{-1}), and initial concentration of phenol (50- 150 mgL^{-1}) were assessed. The stock solution of phenol was prepared with a concentration of 1000 ppm in double distilled water. The optimum pH was then determined by varying the pH in the range of 2-8 and keeping constant the other variables (contact time, adsorbent dose, and initial phenol concentration). The experiments were performed in 100 milliliter beaker with a constant concentration of phenol. Then, this mixture was shacked with a shaker device of enforce model with 150 rpm and the room temperature of 20 – 25°C. The HCl and NaOH were used to adjust the pH solution. In the next step, the optimum adsorbent dose was estimated by keeping constant the contact time and initial phenol concentration and also the obtained optimum pH. After determining the optimum pH and adsorbent dose, the various concentrations of the phenol in the specified times of contact were investigated. The final phenol concentration in the solution was measured by the UV-Visible spectrophotometer at a wavelength 500nm and with regard to standard curve, respectively (20, 21).

The removal efficiency and sorption capacity of the Pistacia mutica were determined by Eq. (1) and (2), respectively (22, 23):

$$R=[\frac{(C_0-C_f)}{C_0}] \times 100 \quad (1) \qquad Qe=\frac{(C_0-C_e)V}{M} \quad (2)$$

Where; R (%) and qe (mg/g) are the removal efficiency and adsorption capacity, respectively. C_0 (mg /L) and C_f are the initial and final concentration, Ce (mg/ L) is concentration at the equilibrium, m (g) is the mass of the adsorbent, and V (L) is the volume of the solution.

2.4.Isotherm and Kinetics

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

Table2. The equation of isotherms (24, 25)

model	equation	
Langmuir	$\frac{c_e}{q_e} = \frac{1}{q_m k_l} + \frac{c_e}{q_m}$	(3)
Freundlich	$\text{Log } q_e = \frac{1}{n} \log c_e + \log k_f$	(4)
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$	(5)
Harkins Jura	$\frac{1}{q_e^2} = \left[\frac{B_{HJ}}{A_{HJ}}\right] - \left[\frac{1}{A_{HJ}}\right] \log C_e$	(6)

Kinetic models are used to examine the rate of adsorption process and the potential rate of controlling step. In the present work, the obtained kinetic data from batch studies were analyzed using the pseudo second-order, Intraparticle diffusion, and pseudo first-order model. The study of kinetic models was conducted in contact time between 10-105 min with aniline and phenol concentration of 50 mg/l and optimum amount of pH and adsorbent dose. To evaluate the differences in the biosorptionrates and uptakes, the kinetic data were described with Intraparticcle diffusion, pseudo first-, and pseudo second-order models. The linearized form of model is shown in Table 3.

Table3. The equation of kinetics (26, 27)

model	equation	
pseudo-first-order	$\text{Log } (q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$	(7)
pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{t}{q_e}$	(8)
Intra-particle diffusion	$q_t = K_{pi} t^{0.5} + c$	(9)

3. Results

3.1.Effect of pH and initial phenol concentration

As is seen in Figure 1, the pH value of the solution was an important controlling parameter in the adsorption process. The effect of pH on phenol uptake in the batch process was studied by varying the pH level from 2 to 8. It was shown in Figure 1 that on the basis of the maximum removals of phenol for contact time of 10 min carried out at pH4, the removal percent of 81.9% was obtained at biosorbent dosage from 0.6 g/L.

To determine the effect of initial phenol concentration on the adsorption process, the initial concentration of phenol was varied from 50 to 150 mg/L at the fixed pH level of 4, adsorbent dose of 0.6g/L, and contact time of 10 min.

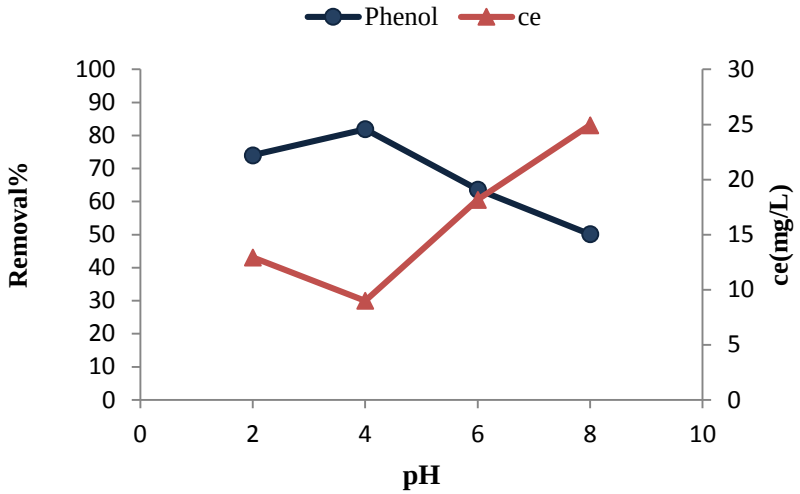


Figure 1. Effect of pH on removal efficiency of phenol
(Contact time =10 min, dosage: 0.6g/L, initial concentration: 50 mg/L)

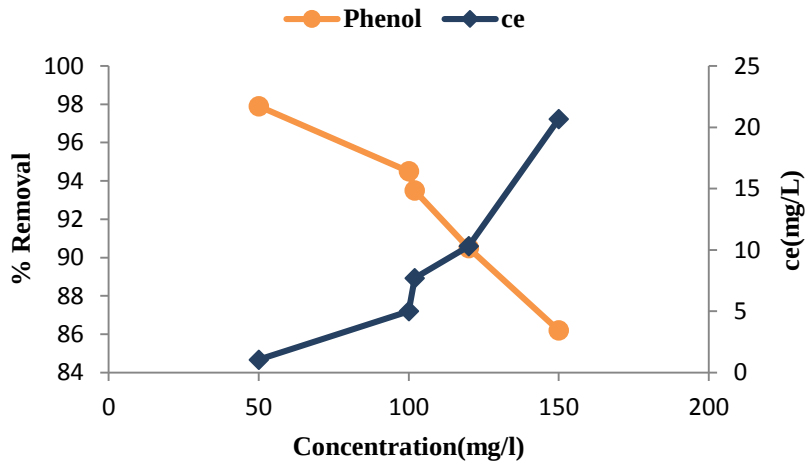


Figure 2. Effect of phenol concentration on removal efficiency of phenol
(Time = 10 min, dosage: 0.6g/l, pH =4)

3.2.Effect of adsorbent dose and contact time

The effect of adsorbent dose on removal of phenol was studied by varying the dose of adsorbent from 0.4 to 1.5 g/L. As shown in Figure 3, the adsorbent dose significantly influenced the amount of adsorbed. In fact, the percentage of phenol removal steeply increased with the adsorbent loading up to 1 g/L, but qe adsorbed decreased as the dose of adsorbent increased from 0.4 to 1.5 g/L. 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 phenol onto the P.mutica constant initial phenol concentration (50 mg/L) and optimum adsorbent dosage and pH. The uptake of phenol on P. atlantica was rapid in the first 45 min (%99), then the adsorption rate finally reached equilibrium in about 60 min.

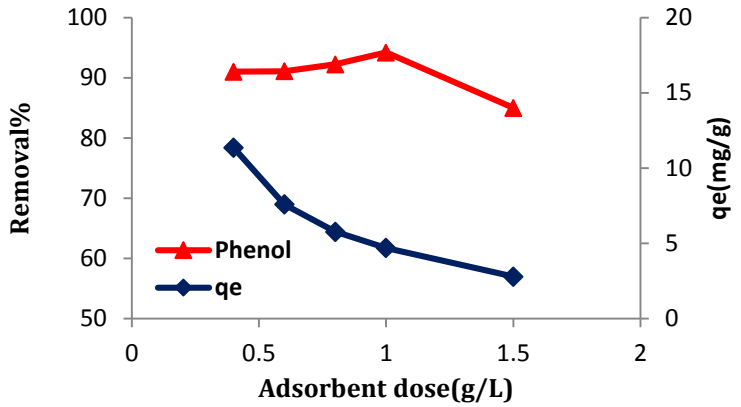


Fig 3. Effect of adsorbent dose on removal efficiency of phenol
(Contact time = 10 min, pH 4, phenol concentration: 50ppm)

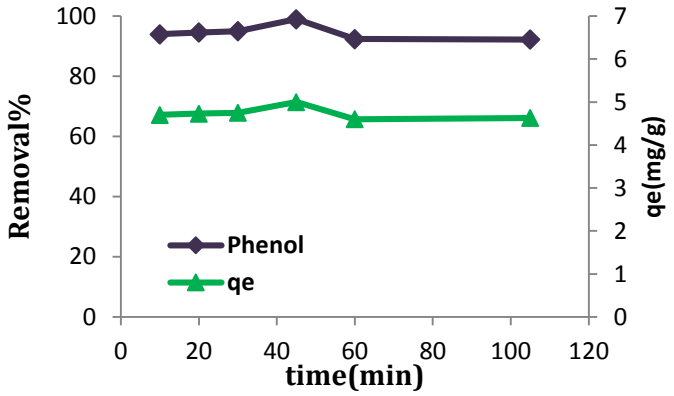


Fig 4. Effect of contact time on removal efficiency of phenol
(pH, dosage and concentration: optimum)

3.3.Adsorption isotherms and kinetics

The results and correlation coefficients for isotherms model are presented in Table 4 and Figure 5. The findings showed that phenol on dried baneh fitted according to Langmuir Model isotherm model (R^2=0.985). Furthermore, it was found to agree with Tempkin isotherm (R^2=0.98) more than with Freundlich (R^2=0.967) and Harkins Jura Models (R^2=0.94).

Table4. The adsorption isotherms constants for the removal phenol

Langmuir				Freundlich		
q_m	R_L	K_L	R^2	n	K_F	R^2
8	0.006	3	0.9847	2.8	8.18	0.9678
Temkin				**Harkins Jura**		
B_T	A_T	b_T(Kj/mol)	R^2	B_{HJ}	A_{HJ}	R2
4.57	5.07 ×10^2	0.55	0.9799	1.5	158.7	0.9406

The results and correlation coefficients for Kinetic Model are presented in Table 5, and Figure 6. 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**.**

Table5. The adsorption kinetic model constants for the removal phenol

	Pseudo second-order			Pseudo First-order			Intra-particle diffusion		
Co(mg/l)	K_2(g/mg min)	Qe(mg/g)	R^2	$K_{1(1/min)}$	Qe(mg/g)	R^2	K_{pi}	c	R^2
Phenol	0.285	50	0.998	0.033	1.6	0.908	0.085	4.4	0.979

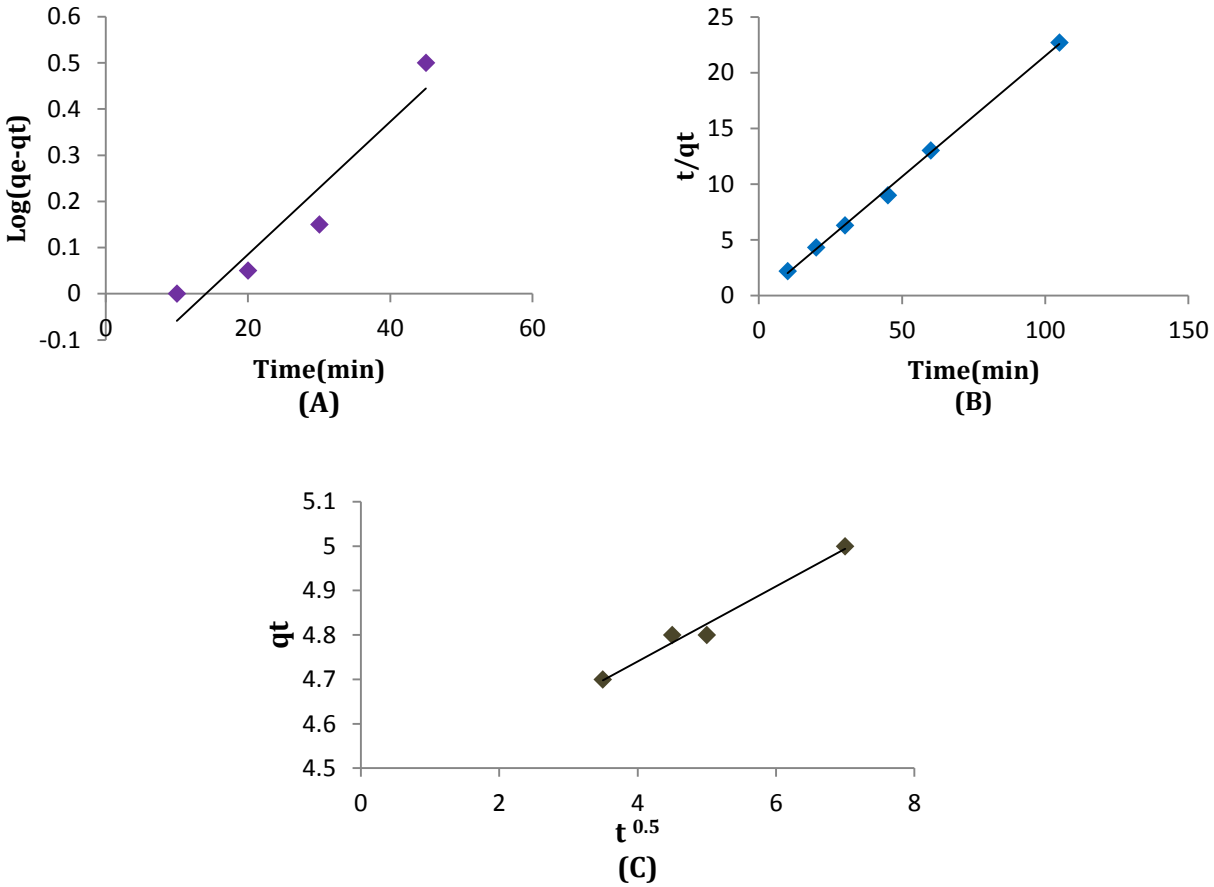


Fig6. Kinetic isotherms (a); pseudo first order (b); pseudo-second-order (c), Intra-particle diffusion

4. Discussion

Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate. Phenol as a weak acid compound with pKa ≈9.5 is dissociated at pH> pKa (1). Therefore, the adsorption decreases at high pH values due to ionization of adsorbate molecules. The reason could also be due to the electrostatic repulsions between the negative surface charge and the phenol anions in solution (22). At the same time, at acidic pH, the percentage removal was higher because phenol was undissociated and the dispersion interaction predominated. This result can be supported by results of various studies (5). Another effective parameter on phenol removal adsorption was

documented to be the initial phenol concentration which has been studied in this work. Initial concentration effect on the adsorption of phenol is shown in Figure 2. By increasing the initial concentration of 50 to 150 mg/L, the removal phenol decreased. This may be due to the limited number of active sites on the adsorbent that becomes saturated at high concentration of phenol. In other words, at low concentrations, the availability of phenol molecules to adsorption sites is more than high concentrations (23). The study of Ahmadi et al. showed that using Baneh, the level of aniline decreased to 81.6% with an increase in removing concentration to 150 mg/L (16) and the adsorption rate decreased by increasing the adsorbent dose from 1 to 1.5 g/L, which was due to the limited number of active sites on the adsorbent and decreasing the active surface of adsorbent (24, 28). The optimum contact time was found to be 45 min which can probably be explained by the greater contact surface of baneh adsorbent, because any increase in the specific surface area could lead to more adsorption percentage in lower time (20,29). The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant, which meant that the uptake process followed the pseudo-second-order expression with correlation coefficients always greater than 0.998. 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 (30,31). Overall, the current study investigated the adsorption of phenol from aqueous solutions onto dried P.atlantica biomass. The results showed that the solution pH played a significant role in influencing the capacity of an adsorbent towards phenol molecules. An increase in the pH of solutions led to a decrease in the sorption capacities of phenol. The sorbed amounts of phenol also increased with any 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 phenol. The pseudo-second-order kinetic model provided the best correlation of the experimental data. The findings of the study also showed that baneh biomass can be effectively used as adsorbent for the removal of phenol from aqueous solutions. Moyo1 et al. in a previous study had also reported the adsorption potential of phenol claiming that the adsorption capacity was greater. Hence, the equilibrium data fitted well to the Langmuir Model with correlating constant (R2) higher than 0.99(32).

Acknowledgments

The authors wish to thank Dr.Ramin Saravani (Clinical Biochemistry) for support of the study.

Conflict of interest

The Authors have no conflict of interest.

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. DOI: 10.1016/0043-1354(95)00060-X
2. An F, Feng X, Gao B. Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO 2. Chemical Engineering Journal. 2009; 151(1):183-7.DOI:10.1016/j.cej.2009.02.011
3. Calace N, Nardi E, Petronio B.M, Pietroletti M. Adsorption of phenols by papermillsludges, Environ. Pollut.ion 2002; 118(3);315–319. DOI: 10.1016/S0269-7491(01)00303-7
4. Akbal F, Onar A.N. Photo catalytic degradation of phenol, Assessment Environ.

Monit. Assess.2003; 83(3); 295–302. DOI:10.3390/w6061785

5. Banat F.A, Al-Bashir B, Al-Asheh S, Hayajneh O. Adsorption of phenol by bentonite, Environ. Pollution .2000; 107(3): 391–398. DOI:10.1016/S0269-7491 (99) 00173-6
6. Ozkaya B. Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models. Journal of Hazardous Materials.2006; 129(1-3): 158–163. DOI:10.1016/j.jhazmat.2005.08.025
7. 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. DOI:10.1016/S0011-9164(02)00220-5
8. 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. DOI:10.1016/j.cej.2011.08.027
9. Pan B, Pan B, Zhang W, Zhang Q, Zhang Q, Zheng S. Adsorptive removal of phenol from aqueous phase by using a porous acrylic ester polymer. Journal of Hazardous Materials. 2008; 157(2-3): 293–299.DOI:10.1016/j.jhazmat.2007.12.102
10. Deng H, Li G, Yang H, Tang J. Preparation of activated carbons from cotton stalk by microwave assisted KOH and K2CO3 activation. Chemical Engineering Journal.2010;163(3):373–381. DOI:10.1016/j.cej.2010.08.019
11. Da'na E, Sayari A. Adsorption of heavy metals on amine-functionalized SBA-15 prepared by co-condensation: Applications to real water samples. Desalination 2012; 285: 62–67. http://doi.org/10.1016/j. desal.2011.09.034
12. Tilaki RA. Effect of glucose and lactose on uptake of phenol by lemnaminor. Iranian Journal of Environmental Health Science & Engineering. 2010; 7(2):123-8.
13. Won S.W, Kim H, Choi S, Chung B, Kim K, Yun Y. Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of Corynebacteriumglutamicum as a low-cost biosorbent. Chemical Engineering Journal.2006;121(1);37–43. DOI:10.1016/j.cej.2006.04.005
14. Batzias F, Sidiras D, Schroederb E, Weber C. Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems. Chemical Engineering Journal. 2009;148(2-3):459–472. DOI: 10.1016/j .cej.2008.09.025
15. Ahmedna M, Marshall W.E, Rao R.M.Production of granular activated carbons from selected agricultural by-products and evaluation of their physical,chemical and adsorption properties, Bioresource Technology.2000;71(2):113–123. DOI: 10.1016/S0960-8524(99)00070-X
16. Ahmadi Sh, Kord Mostafapour F. Adsorptive removal of aniline from aqueous solutions by Pistacia atlantica (Baneh) shells: isotherm and kinetic studies. Journal of Science, Technology and Environmental Informatics. 2017; 05(01): 327-335. DOI:10.18801/jstei.050117.35
17. Pourreza M , Shaw J.D, Zangeneh H. Sustainability of wild pistachio (Pistacia atlantica Desf.) in Zagros forests, Iran Forest Ecology and Management.2008; 255: 3667–3671. DOI:10.1016/j.foreco.2008.01.057
18. Masoud-Nejabat M, Negahdrsaber M, Ghahari G. Range of soil and climate characteristics appropriate for Pistacia atlantica forest development and rehabilitation (case study: Fars province, Iran).Journal of water and land developments of Section of Land Reclamation and Environmental Engineering in Agriculture.2017;32 (1–3): 71–78 . DOI: 10.1515/jwld-2017-0008
19. Zazouli MA, Balarak D, Mahdavi Y. Pyrocatechol Removal from Aqueous Solutions by Using Azolla Filiculoides. Health Scope. 2013; 2(1):1-6. DOI: 10.17795/jhealthscope-963
20. Ahmadi sh, Kord Mostafapoor F. Adsorptive removal of Bisphenol A from aqueous solutions by Pistacia atlantica: isotherm and kinetic Studies. The Pharmaceutical and Chemical Journal2017; 4(2):1-8.
21. Akbartabar I, Yazdanshenas ME, Tayebi H, Nasirizadeh N. Investigation of Acid Blue 62 dyeadsorption using SBA-15/Polyaniline mesoporous nan composite: Kinetic and Thermodynamic study .Iranian Journal of Health Sciences.2017; 5(3):17-34.
22. Ahmadi Sh, Kord Mostafapour F, Bazrafshan E. Removal of Aniline and from

Aqueous Solutions by Coagulation/Flocculation Flotation. Chemical Science International Journal.2017;18(3):1-10. DOI: 10.9734/CSIJ/2017/32016

23. Ahmadi sh, Kord Mostafapour F. Survey of Efficiency of Dissolved Air Flotation in. Removal Penicillin G Potassium from Aqueous Solutions. British Journal of Pharmaceutical Research. 2017; 15(3): 1-11. DOI: 10.9734/BJPR/2017/31180
24. Ahmadi S, Banach A, Kord Mostafapour F, Balarak D. Study survey of cupric oxide nanoparticles in removal efficiency of ciprofloxacin antibiotic. Desalination and Water Treatment .2017; 89:297–303. Doi: 10.5004/dwt.2017.21362.
25. Ahmadi Sh, Bazrafshan E, Kord Mostafapour. Treatment of landfill leachate using a combined Coagulation and modify bentonite adsorption processes. Journal of scientific and Engineering Research 2017; 4(2):58-64.
26. Ahmadi S.H, Kord Mostafapour F. Tea waste as a low cost adsorbent for the removal of COD from landfill leachate: Kinetic Study. Journal of Scientific and Engineering Research.2017; 4(6):103-108.
27. DiyanatiTilaki R.,Balarak D, Ghasemi M. Survey of Efficiency Agricultural Weast in Removal of Acid Orang 7(AO7) Dyes from Aqueous Solution: Kinetic and Equilibrium Study. Iranian journal of health sciences .2014;2(1):51-61.
28. Rahdar S, Ahmadi Sh. Removal of Phenol and Aniline from Aqueous Solutions by Using Adsorption on to Pistacia terebinthus: Study of Adsorption Isotherm and Kinetics. Journal of Health Research in Community. 2017; 2(4): 35-45.
29. Samadi M.T, Kashitarash Esfahani Z, Ahangari F, Ahmadi Sh, Jafari J. Nickel removal from aqueous environments using carbon nanotubes, Journal Water and Waste. 2013; 24: 38–44.
30. Balanay JA, Bartolucci AA, Lungu CT. Adsorption characteristics of activated carbon fibers for toluene: application in respiratory protection. Journal of Occupational and Environmental Hygiene 2014;11(3):133-43. Doi: 10.1080/15459624.2013.816433.
31. Radhika M, Palanivelu K. Adsorptive removal of chloro phenols from aqueous solution by low cost adsorbent: Kinetics and isotherm analysis. Journal of Hazardous Materials.2006;138(1):116–119. /10.1016/j.jhazmat.2006.05.045
32. Moyo M, Mutare E, Chigondo F, C. Nyamunda B. Removal of phenol from of aques solution by adsorption on yeast, saccharomyces cerevisiae ijras. International Journal of Recent Research and Applied Studies. 2012; 11 (3):486-494.