



Efficiency in phenol removal from aqueous solutions of pomegranate peel ash as a natural adsorbent

Ali Asghar Najafpoor¹, Sina Dousti^{2*}, Ahmad Joneidi Jafari³, Ahmad Hosseinzadeh⁴

¹Associate Professor, Health Sciences Research Center, Department of Environmental Health Engineering, School of Health, Mashhad University of Medical Sciences, Mashhad, Iran

²MSc in Environmental Health Engineering, Student Research Committee, School of Health, Mashhad University of Medical Science, Mashhad, Iran

³Professor of Environmental Health Engineering, Department of Environmental Health Engineering, Center for Environmental Health Technology, School of Health, Iran University of Medical Sciences, Tehran, Iran

⁴MSc Student of Environmental Health Engineering, Student Research Committee, Department of Environmental Health Engineering, School of Health, Mashhad University of Medical Sciences, Mashhad, Iran

Abstract

Background: Phenol is an organic pollutant found in industrial effluents that is very toxic to humans and the environment. This study used pomegranate peel ash as a natural adsorbent to remove phenol from aqueous solutions.

Methods: In this study, pomegranate peel ash in different doses was used as a new adsorbent for the removal of phenol. The effects of contact time, pH, adsorbent dose and initial phenol concentration were recorded. Then, the adsorption data was described with Langmuir and Freundlich adsorption isotherms; Excel software was used for data analysis.

Results: The highest percentage of phenol adsorption was observed at pH=7. The optimum amount of adsorbent was 0.6 g/l, and after 120 minutes, the process reached an equilibrium state. The adsorption of phenol decreased following an increase in the pH of the solution. It was also observed that contact time significantly affected the rate of phenol adsorption. The experimental data fit much better in the Freundlich ($R^2=0.9056$) model than in the Langmuir ($R^2=0.8674$) model.

Conclusion: Pomegranate peel ash has the potential to be utilized for the cost-effective removal of phenol from aqueous solutions.

Keywords: Phenol removal, Pomegranate peel ash, Aqueous solution

Citation: Najaf Poor AA, Dousti S, Joneidi Jafari A, Hosseinzadeh A. Efficiency in phenol removal from aqueous solutions of pomegranate peel ash as a natural adsorbent. *Environmental Health Engineering and Management Journal* 2016; 3(1): 41–46.

Article History:

Received: 1 February 2016

Accepted: 29 February 2016

ePublished: 13 March 2016

*Correspondence to:

Sina Dousti

Email: sina_dosty@yahoo.com

Introduction

The presence of phenol and its derivatives in water and wastewater is a major concern because of their hazards to human health and the environment. Phenol enters the environment naturally from the decomposition of algae and plants; however, the presence of phenolic compounds in surface waters is caused mainly by industrial wastewaters (1). Phenolic compounds comprise one of the most common groups of pollutants in wastewaters produced by resins, plastics, explosives, steel, leather, etc. Organic contaminants that enter bodies of water in various concentrations are able to react with phenolic compounds and produce chlorinated phenolic compounds. Phenol is known to be a solvent and an antiseptic substance and is used as an additive to increase the efficiency of disinfection processes; such chlorinated substances can also be produced through processes (1,2). The Environmental Protection Agency

(EPA) classifies these compounds as one of the most important groups of priority pollutants because of their high toxicity, carcinogenic properties, bioaccumulation, and low biodegradation potential, and the adverse effects they have on human life (1-3). Health effects resulting from exposure to phenol are dependent upon absorption rate and exposure time. These effects range from mucosal and skin irritation, systemic toxicity, decreased blood pressure, and increased heart rate to coma (4). One study showed that the consumption of between 8 and 15 mg of phenol can lead to death in humans (5). Additionally, phenolic compounds in drinking water resources disinfected by chlorine compounds may create chlorophenol compounds. These substances may make some undesirable changes in the odor and taste of water, making it unsuitable for consumption (6). Moreover, phenol is considered to be a major carcinogenic agent. Even low concentrations of it



may lead to significant health concerns. Phenol can penetrate cells and cause cytoplasmic coagulation; phenolic contaminants can damage sensitive cells (7-9). Therefore, the detection, identification, and determination of phenolic compounds in wastewaters are very important. The proportion of such pollutants in industrial wastewaters has to be considered before the wastewater is discharged into water flows. Based on the aforementioned reasons, the EPA has determined a maximum concentration of 1 mg/L for phenol in industrial effluents discharged into surface waters (10,11).

Various processes are used for the removal of phenolic compounds from aqueous solutions, including extraction, activated carbon adsorption, distillation with steam, electrochemical methods, irradiation, advanced oxidation, chemical oxidation, adsorption, and biological treatments. Most of these methods have disadvantages such as the high cost of treatment or the need for additional treatments. None of these approaches have been successful in completely removing phenol compounds from aqueous solutions; each suffers from one or more limitations, such as the high cost, the need for additional treatment, the production of dangerous byproducts, low efficiency, and limited applicability to various concentrations of pollutants (12).

Extensive research has been carried out to study the phenol removal potential of each method. Many biological and non-biological processes, such as polymerization, electrocoagulation, extraction, photo-decomposition, advanced oxidation process, and adsorption, have been employed by various researchers for phenol removal. The enzyme horseradish peroxidase has been used for phenol polymerization. In optimal conditions, a phenol polymerization efficiency of about 90% was observed. During electro-coagulation, phenol was removed by the combined effects of sweep coagulation and adsorption. At a high current density and a solution pH of 7, the remarkable removal rate of 92% after 2 hours was achieved. Adsorption by various adsorbents is another attractive alternative. It is advantageous that a wide range of adsorbents are available. Many adsorbents are waste materials from agricultural and other industrial operations, such as distilleries. Phenol removal rates ranging from 88% to 95% have been observed using various adsorbents. Adsorption seems to be the most widely-studied operation for phenol removal (13).

The adsorption process, one of the most important methods, is widely used for the removal of organic and inorganic pollutants from aqueous solutions (14). Different adsorbents have been used for the removal of phenol from aqueous solutions; among them, commercial activated carbon has a great ability to absorb phenol from aquatic environments, although carbon production and its regeneration process has a high cost. Therefore, the economic aspects of adsorption processes need to be considered. In recent years, researchers have attempted to replace commercial activated carbon with low-cost adsorbents (15). The present study investigated the performance and ef-

iciency of ash made from pomegranate peel for the removal of phenol from aqueous solutions.

Notably, this is the first time pomegranate peel ash as a natural adsorbent for phenol removal is being studied.

Methods

Preparation of adsorbent

To produce the pomegranate peel ash, pomegranate skins were washed with distilled water to remove impurities and then dried at 105°C for 24 hours. The dried pomegranate peels were burned at 500°C for 2 hours to be turned into ash. Then the chopped dried skin was poured into a Chinese plant. Ash was produced after crushing operations by standard sieves ranging between 60- and 200-mesh sizes. The prepared adsorbent was poured into a closed container. No other chemical or physical operation was performed before adsorption on the adsorbent.

Preparation of phenol solution

All analytical grade chemicals used in the present study were provided by Merck. Phenol specific for laboratory analysis was purchased with a purity of 99.9% and a molecular mass of 94.11 g/mol. To prepare the stock solution (1000 mg/L), the required amount of phenol was dissolved in distilled water. Solution concentrations for the experiments were obtained by diluting the stock solution. Because of the volatile nature of phenol, all precautions were taken to prevent its evaporation from the samples during preparation and subsequent experiments. Normal HCL and NaOH 0.1 were applied for pH adjustment.

Adsorption experiments and analysis of samples

Phenol was measured with a spectrophotometer (Model T80 UV/VIS) at a wavelength of 500 nm. At first, the calibration curve was constructed by assaying standard solutions of phenol in concentrations of 5 to 100 mg/L; then the phenol concentrations of samples were calculated based on the obtained curve (16,17).

The effects of various parameters, including initial pH, adsorbent dose, contact time, and initial phenol concentration, on phenol removal were investigated. All tests were accomplished at room temperature (23 ± 2°C). Experiments were performed in a closed flask of 250 mL capacity and on a magnetic shaker. In the experiments, a specific proportion of adsorbent was added to flasks containing 100 mL sample and stirred at 120 rpm. After the contact time elapsed, all samples were filtered through Whatman filter paper (No. 42), phenol concentrations in the filtrated solutions were measured, and the amount of phenol adsorbed (mg/g) was calculated using the following equation. Final results are reported as the average of the two measurements. The range of variables is presented in Table 1.

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

where, C_0 = is the initial concentration of phenol, C_e = is the phenol concentration after the test was performed and

Table 1. Range of parameters examined in this study

Contact time (min)	Temperature (°C)	The concentration of phenol (mg/L ⁻¹)	Dose of adsorbent (g/L ⁻¹)	pH
15, 30, 60, 90, 120, 150, 180, 210	23±2°	10, 20, 30, 40, 50, 80, 100	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7	2-12

a state of balance was achieved, V = is the volume of the solution (L), and M = is the amount of adsorbent used (g).

Adsorption isotherm

The equilibrium isotherms are very important in designing adsorption systems. To estimate the adsorption characteristics of an adsorbent, the isotherm adsorption of that adsorbent with a specific adsorbate is accomplished. The concentration variation method was used to calculate the adsorption characteristics of the adsorbent and the process. It is mainly carried out by selecting an appropriate concentration range of the adsorbate with a fixed mass of adsorbent. The ratio of the adsorbent mass and the volume of the dye solution were applied. For this purpose, two adsorption models (Langmuir and Freundlich) were used.

Langmuir Isotherm

The Langmuir equation is based on the assumption that the maximum adsorption occurred because of a saturated monolayer of adsorbate molecules on the adsorbent surface (18). The non-linear equation of the Langmuir isotherm is as follows:

$$\text{Original equation: } q_e = \frac{q_m b C_e}{1 + b C_e}$$

$$\text{Linearized equation: } \frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m}$$

Freundlich Isotherm

The Freundlich isotherm is based on multilayer adsorption on the heterogeneous surface of the adsorbent containing an unequal amount of energies. It is not limited to a monolayer adsorption, but is also applied for multilayer adsorption. The non-linear equation of the Freundlich isotherm is shown below (18), and the linearized and original equations of these models are as follows:

$$\text{Original equation: } q_e = k_f C_e^{\frac{1}{n}}$$

$$\text{Linearized equation: } \ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

where q_e is the ratio of adsorbed adsorbate per specific adsorbent (mg/g), C_e is the residual adsorbate concentration (mg/L), n is the constant of the Freundlich equilibrium related to bond energies between the adsorbate and the adsorbent, k_f is the constant of the Freundlich equilibrium indicative of bond strength (mg/g), q_m is the proportion of the required adsorbate to form a monolayer (mg/g), and b is the constant of the Langmuir equilibrium indicative of the energy of adsorption (l/mg).

Analysis and statistical methods

Statistical analysis was done using SPSS software version

19 for windows. In addition, the coefficients of these two models along with the correlation coefficients (R^2) were calculated in Excel software. The results for these equations were fitted and their goodness of fit was evaluated.

Results

Effect of pH on adsorption efficiency

To determine the effects of initial pH on phenol adsorption by pomegranate peel ash and the optimal pH, phenol adsorption was surveyed as a function of hydrogen ion concentration. In each series of test samples, the initial pH was determined to be in the range of 2-12, adsorbent at 0.4 g per 100 mL was used, and the initial phenol concentration in all samples was 50 mg/L. Figure 1 shows the effect of initial pH on the performance by of pomegranate skin ash on phenol adsorption. As clearly indicated in the graph, the highest removal of phenol occurred in pH = 7.

Effect of adsorbent dose

As can be seen in Figure 2, there is a direct relationship between adsorbent dose and phenol removal efficiency. Phenol removal percentages increased from 69.8% to 97.06% at adsorbent doses of 0.1 and 0.7 g/L, respectively. However, the proportion of adsorption capacity was considered as the phenol adsorbed per gram of adsorbent re-

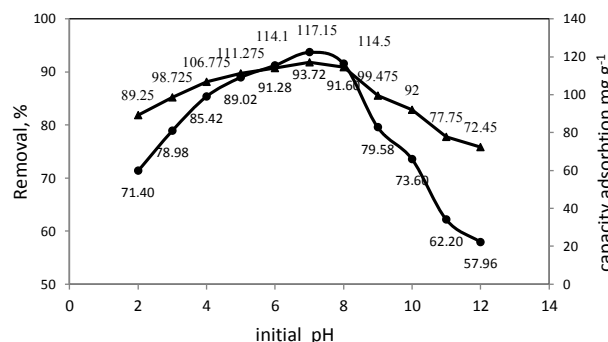


Figure 1. Effect of initial pH on phenol adsorption by pomegranate peel ash

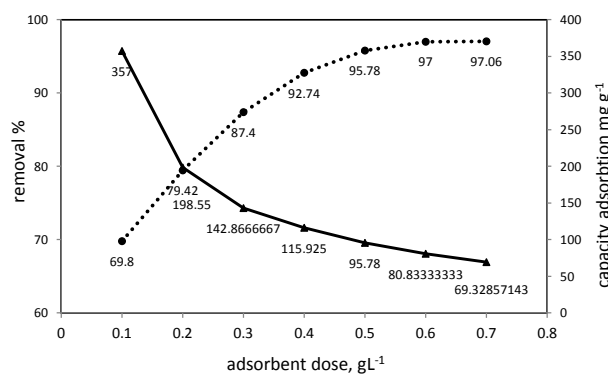


Figure 2. Effect of adsorbent dose on phenol adsorption by pomegranate peel ash.

duced. Based on the results, the adsorbent dose of 0.6 g/L was chosen as the optimal dose of adsorbent and was used in other parts of the study.

Effect of contact time

The effect of contact time on the adsorption process at the initial phenol concentration of 50 mg/L and 0.6 g/L of the adsorbent dose was conducted for times of 15 to 210 minutes. As Figure 3 shows, adsorption capacity and the percentage of phenol removal by adsorbent have a significant direct relationship with contact time in the early stages of adsorption. The highest elimination efficiency (95% to 96%) and adsorption capacity (79 to 97 mg/g) were obtained after 120 minutes. Therefore, an exposure time of 120 minutes was selected as the optimal equilibrium time.

Effect of initial phenol concentration:

As shown in Figure 4, the results show that when the initial phenol concentration increases from 10 to 100 mg/L, adsorption capacity of 16 mg/g increases from 10 to 148 mg/g, while the removal of phenol at the same time shows a reverse trend.

Table 2 shows the parameters of the isotherm and kinetic equations in phenol adsorption by pomegranate peel ash. As shown in Table 2, the phenol adsorbed into the pomegranate peel ash can be described by both Freundlich and Langmuir isotherms (Figures 5 and 6).

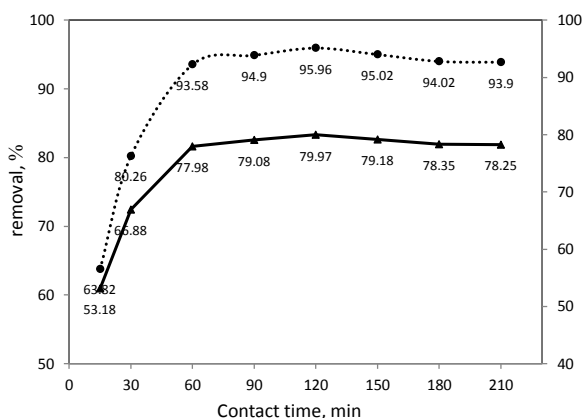


Figure 3. Effect of contact time on phenol adsorption by pomegranate peel ash.

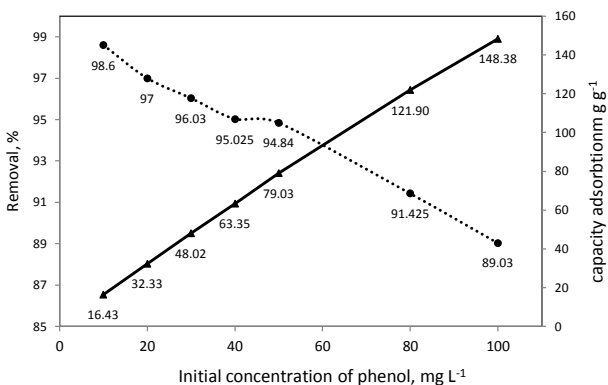


Figure 4. Effect of initial phenol concentration on phenol adsorption by pomegranate peel ash.

Table 2. Parameters regarding the adsorption isotherm models for phenol adsorption on pomegranate peel ash temperature of 23 ± 2°C

Langmuir isotherm			Freundlich isotherm		
q_m (mg g ⁻¹)	K_L (L kg ⁻¹)	R^2	K_f	n	R^2
344.86	0.143	0.8674	48.41	1.516	0.9056

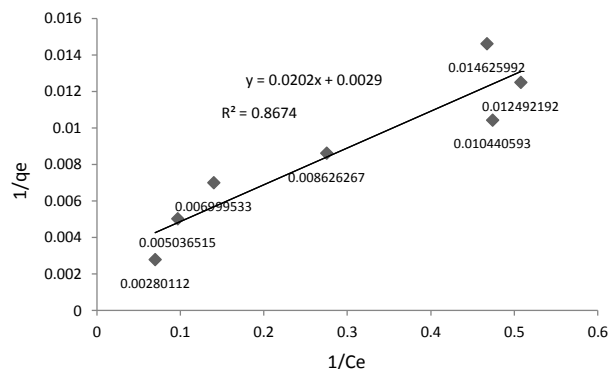


Figure 5. Langmuir isotherm for phenol adsorption by pomegranate peel ash ($R^2 = 0.8674$).

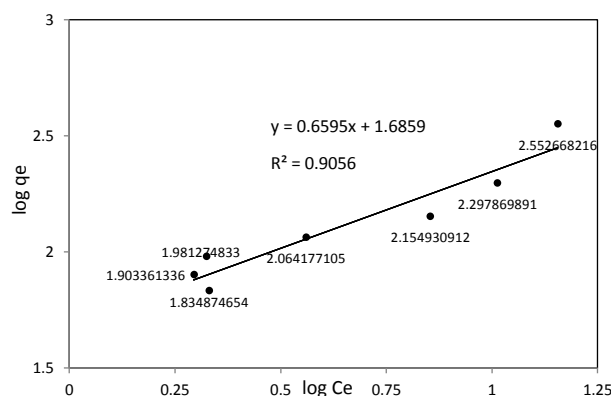


Figure 6. Freundlich isotherm for phenol adsorption by pomegranate peel ash ($R^2 = 0.9056$).

Discussion

The effect of pH on adsorption efficiency plays an important role in the process of adsorption and also has a key role in absorption capacity (19). In general, removal efficiency decreases have been reported in low and high pH values (20).

The direct relationship between pH and phenol removal efficiency may be caused by the presence of H⁺ ions. Since phenol ions can be neutralized by the hydrogen ions, their adsorption is reduced on polar adsorbents. Moreover, the process efficiency is reduced when pH is increased above 7. This reduction in efficiency at higher pH values may be because of the fact that at a higher pH, phenol is in the form of salt and loses its negative charges. Thus, the adsorption of phenol will face serious difficulties. In addition, OH ions inhibit the absorption of phenol by the adsorbent (17). Rengaraj et al studied the removal of phenol by palm kernels, and their results agree with the results of the present study (20).

Effects of adsorbent dose

One of the most important parameters of the adsorption process is adsorbent dose. As shown in Figure 2, the percentages of phenol removal with increases in the amount of adsorbent experienced an upward trend. This can indicate that there are still active sites on the surface of the adsorbent that are unsaturated. Data from this study indicated clearly that the greater the rate of adsorbent was, the more efficient phenol removal would be. This could be because an increase in the proportion of adsorbent provides more active surface area for adsorption. Thus, when more adsorbent is added, the remaining amount of pollutants will stay constant. The results showed that the phenol elimination efficiency encountered no changes at adsorbent doses higher than 0.6 g/L (21). Although phenol removal efficiency increased with increasing doses of adsorbent, the amount of phenol adsorbed per gram adsorbent decreased. Because of absorption by active sites, the concentration of the phenol solution reduced the saturated adsorbent surface. Conversely, increasing the amount of adsorbent caused aggregation and adhesion to them (2).

Effects of contact time

Contact time is one of the most important parameters in determining the adsorption process equilibrium time. The results showed that at first, the removal of adsorbing phenolic compounds was high. However, the removal efficiency was gradually reduced because of the equilibrium time. This phenomenon can be attributed to the abundance of available spaces in the adsorbent at first. Over time, because of the repulsive force between the molecules of the adsorbent and the liquid phase, the remaining empty spaces of the adsorbent surface are hardly occupied. Similar findings have been reported by Calvete et al (22), Cengiz and Cavas (23), and SenthilKumar et al (24).

Effects of initial phenol concentration

The direct relationship between initial phenol concentration and phenol removal efficiency is interpreted as follows: the mass transfer driving force is increased with the rise of phenol concentration, and thus soluble phenolic molecules flow to the planchette liquid adsorbent layer. Finally, the adsorbent surface increases (25,26). The reduction in phenol removal efficiency that occurs over this process may be owing to the decrease in active sites of the adsorbent surface. Similar results for phenol adsorption from aqueous solutions by clay and other adsorbents have been recorded (27-30).

Conclusion

Adsorption is known as a vigorous and well-established procedure for treating industrial effluents. This study investigated the potential of pomegranate peel ash as an adsorbent in removing phenol from aqueous solutions. The effects of the four variables of initial pH, contact time, adsorbent dose, and phenol concentration as well as the adsorption isotherm were studied. The results indicated that the highest rate of phenol adsorption was observed

at pH = 7, the optimum amount of adsorbent was 0.6 g/L, and the process reached the state of equilibrium after 120 minutes. Based on the results of the current study, pomegranate peel ash has a good potential for the removal of phenol from aqueous solutions.

Acknowledgments

This project was financially supported by the Faculty of Public Health, Mashhad University of Medical Sciences. The authors are grateful to the head of the Environmental Chemistry Laboratory for his help.

Ethical issues

The authors certify that all data collected during the study period are presented in this manuscript, and no datum from this study has been or will be published separately.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AAN conceived the study and supervised development of work, helped in data interpretation and manuscript evaluation. SD designed and Performed analysis on all samples, interpreted data, wrote manuscript and acted as corresponding author. AJJ helped in data interpretation and manuscript evaluation. AH helped to evaluate and edit the manuscript.

References

1. Yapar S, Ozbudak V, Dias A, Lopes A. Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium-bentonite. *J Hazard Mater* 2005; 121(1-3): 135-9.
2. Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: a short review of recent developments. *J Hazard Mater* 2008; 160 (2-3): 265-88.
3. Ersoz A, Denizli A, Sener I, Atilir A, Diltemiz S, Say R. Removal of phenolic compounds with nitrophenol-imprinted polymer based on pi-pi and hydrogen-bonding interactions. *Separation and Purification Technology* 2004; 38(2): 173-9.
4. Karel V. *Handbook of Environmental Data on Organic Chemicals*, Vol 2. 4th ed. Canada: John Wiley and Sons Inc; 2000.
5. Raynold J, Martindale EF. *The Extra Pharmacopocia Disinfectants and Antiseptics*. 28th ed. Landan; 1982.
6. Rengaraj S, Moon SH, Sivabalan R, Arabindoo B, Murugesan VJ. Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat. *Hazard Mater* 2002; 89(2-3): 185-96.
7. Bódalo A, Gómez E, Hidalgo AM, Gómez M, Murcia MD, López I. Nanofiltration membranes to reduce phenol concentration in wastewater. *Desalination* 2009; 245(1-3): 680-6.
8. Aksu Z, Yener J. A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbent. *Waste Manage* 2001; 21(8): 695-702.
9. Viraraghavan T, De Maria Alfaro F. Adsorption of phenol

- from wastewater by peat fly ash and bentonite. *Hazard Mater* 1998; 57(1-3): 59-70.
10. Balasubramanian A, Venkatesan S. Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid [BMIM]⁺[PF6]⁻ in Tributyl phosphate. *Desalination* 2012; 289: 27-34.
 11. Parliamentary Office Affairs. The environment laws and regulations. Tehran: EPA Publications; 2001.
 12. Li HQ, Han HJ, Du MA, Wang W. Removal of phenols thiocyanate and ammonium from coal gasification wastewater using moving bed biofilm reactor. *Bioresour Technol* 2011; 102(7): 4667-73.
 13. Kulkarni SJ, Kaware JP. Review on research for removal of phenol from wastewater. *International Journal of Scientific and Research Publications* 2013; 3(4): 1-5.
 14. Nevskaja DM, Santianes A, Muñoz V, Guerrero-Ruiz A. Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study. *Carbon* 1999; 37(7): 1065-74.
 15. Lin K, Pan J, Chen Y, Cheng R, Xu X. Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders. *Hazard Mater* 2009; 161(1): 231-240.
 16. Glesceria LA, Greenberg E, Eaton AD. *Standard Methods for the Examination of Water and Wastewater*. 31st ed. Washington DC: APHA; 2005.
 17. Rasoulifard MH, Taheri Ghazvini N, Farhangnia E, Heydari A, Doost Mohammadi S. Removal of direct yellow 9 and reactive orange 122 from contaminated water using chitosan as a polymeric bioadsorbent by adsorption process. *Color Science and Technology* 2010; 4: 17-23. [In Persian].
 18. Abedini S, Alipour V. Cadmium removal from synthetic wastewater by using *Moringa oleifera* seed powder. *Environmental Health Engineering and Management Journal* 2015; 2(4): 157-63.
 19. Rengaraj S, Moon SH, Sivabalan R, Arabindoo B, Murugesan V. Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon. *Waste Manage* 2002; 22(5): 543-8.
 20. Rengaraj S, Sivabalan R, Arabindoo B, Murugesan V. Adsorption kinetics of o-cresol on activated carbon from palm seed coat. *Indian Journal of Chemical Technology* 2000; 7: 127-31.
 21. Chakravarty P, Sarma NS, Sarma HP. Removal of lead(II) from aqueous solution using heartwood of *Areca catechu* powder. *Desalination* 2010; 256(1-3): 16-21.
 22. Calvete T, Lima EC, Cardoso NF, Dias SLP, Pavan FA. Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for the removal of Procion Red MX 3B from aqueous solution—kinetic, equilibrium, and thermodynamic studies. *Chem Eng J* 2009; 155(3): 627-36.
 23. Cengiz S, Cavas L. Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var *cylindracea*. *Bioresour Technol* 2008; 99(7): 2357-63.
 24. SenthilKumar P, Ramalingam S, Sathyaselvabala V, Dinesh Kirupha S, Sivanesan S. Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination* 2011; 266(1-3): 63-71.
 25. Caturla F, Martín-Martínez JM, Molina-Sabio M, Rodríguez-Reinoso F, Torregrosa R. Adsorption of substituted phenols on activated carbon. *J Colloid Interface Sci* 1988; 124(2): 528-34.
 26. Imagawa A, Seto R, Nagaosa Y. Adsorption of chlorinated hydrocarbons from air and aqueous solutions by carbonized rice husk. *Carbon* 2000; 38(4): 628-630.
 27. Nayak PS, Singh BK. Removal of phenol from aqueous solutions by sorption on low cost clay. *Desalination* 2007; 207(1-3): 71-9.
 28. Bhatnagar A. Removal of bromophenols from water using industrial wastes as low cost adsorbents. *J Hazard Mater* 2007; 139(1): 93-102.
 29. Ghaedi M, Tashkhourian J, Amiri A, Sadeghian B. Equilibrium, kinetic and thermodynamic study of removal of reactive orange 12 on platinum nanoparticle loaded on activated carbon as novel adsorbent. *J Chem Eng* 2011; 28(12): 2255-61.
 30. Najafpoor AA, Vojoudi Z, Dehghani MH, Changani F, Alidadi H. Quality assessment of the Kashaf river in north east of Iran in 1996-2005. *J Applied Sciences* 2007; 7(2): 253-7.