RESEARCH ARTICLE

Evaluation of Phenol Removal from Aqueous Solution by Banana Leaf Ash

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Abstract

Several industries such as crude oil refineries, petrochemical plants, processing of olive oil, pesticide manufacturing, and oil and sewage activities produce significant amounts of phenol and its derivatives that are among the most important toxic compounds present in industrial wastewater. The present study was conducted to evaluate the absorption potential of phenol from aqueous solutions using the banana leaf ash (BLA). In this basic-applied research, the banana leaf ash (0.1- 1 g) was used as an absorbent according to the purposes intended in laboratory scale and in batch system, and then changes of phenol concentration effect, pH, contact time and Freundlich and Langmuir adsorption equations were investigated. The removal efficiency was 88.93% at pH of four, initial concentration of 10 mg/L and the contact time of 75 minutes. The Langmuir and Freundlich adsorption isotherms were studied to assess the adsorption equilibrium reactions, which the results demonstrated better compliance of adsorption equilibrium reactions with the Freundlich adsorption isotherm (R^2 0.900) compared to the Langmuir adsorption isotherm (R^2 0.758). Based on the findings of the present study, the banana leaf ash is an inexpensive absorbent with high absorption potential and appropriate ability to the removal of phenol from water and wastewater samples.

Keywords: *Phenol removal, Banana Leaf Ash, Aqueous Solution, Adsorption, Adsorbent*

Introduction

Phenol, C_6H_6O, with a molecular weight of 94.11 g/mol is an aromatic hydrocarbon and from benzene derivatives, which is colorless or white solid in its pure form (1, 2),

hygroscopic and crystalline. It has a very high solubility in water and after dissolving in water makes it very little acidic (2). Phenol is widely used in industrial processes including petrochemical and chemical industries, such as the manufacture of plastics, explosives, production of insulation, industrial adhesives, perfumes, soaps, paints, detergents and disinfectants, wood protection agents, preservatives and pharmaceutical production (3, 6, 8).

Phenol and its derivatives are widespread among the compounds that are imported into water resources naturally in addition to artificial routes (5). This substance is produced naturally in some foods, in human and animal wastes, and in decomposition of organic matter, algae and plants (4, 10). It is widely regarded as environmental pollutant, which exists in different concentrations in wastewater disposal of many industrial processes including coking, synthetic rubber, plastics, paper, oil refineries, petrochemical plants, ceramics, steel, phenolic and industrial resins conversion processes (13, 14).

According to phenol features such as solubility in water and stability in the environment, this combination remains for a long time in the environment and is able to transfer to long distances through water resources (1). Researchers have shown the presence of organic compounds like phenols in groundwater (2, 15). Phenol and its derivatives appear to be major organic pollutants in the world in current century (24). Epidemiological data have been limited on phenol (13).

Phenol is among resistant and toxic compounds in the environment, which causes health and environmental problems frequently (4, 10, 13). Phenolic compounds due to special features such as toxicity, effects on the taste and smell of water, and adverse effect on human health and living organisms are classified as priority pollutants by the United States Environmental Protection Agency (EPA or sometimes USEPA) (16, 9). The priority pollutants are organic or inorganic compounds with known or suspected roles in

carcinogenic and mutagenic effects, or detoxified and severe damage to the fetus (1, 4, 20). Phenols are considered as priority pollutants due to the characteristics of toxicity and carcinogenicity, which are harmful to living organisms even at low concentrations (12, 19, 22).

There are reports on phenol and its derivatives related to severe acute and chronic toxic effects on human health, including a wide range of symptoms: headache, vomiting, liver and kidney damages, seizures, convulsions, cyanosis, eye irritation, damage to skin and other psychiatric disorders (7, 21, 25). Ministry of Environment and Forests (MOEF) of India and the USEPA have placed phenol on the list of pollutants (2, 7).

The MOEF has considered the maximum concentration of 1mg/l phenol for industrial output to surface waters (2, 23). The standard of Environmental Protection Agency of Iran for discharging the phenol is as follows: the maximum allowable concentration of phenol discharge to surface water, agricultural and irrigation use is 1mg/l and to absorbent wells is trace (2). The EPA is demanding the reduction of phenol content in wastewater to less than 1mg/L (16).

According to the World Health Organization (WHO), the acceptable allowable concentration of phenolic compounds in drinking water is estimated at 0.0011 mg/L (23, 25). Since phenol is on the list of priority pollutants with the concentration of <0.5 µg/L in drinking water according to USEPA (17), so the Institute of Standards and Industrial Research of Iran has specified phenol concentration of 0.5µg/L in drinking water (16).

Three various physical, chemical and biological techniques can be used for the removal of phenol (26), such as adsorption (27), wet peroxide oxidation (28), wet air oxidation (29), ozonation (30), aerobic and anaerobic biological reduction, ion exchange in resins, reverse osmosis, solvent extraction, steam distillation and irradiation (26, 31). This pollutant is a toxic substance,

and can be difficulty reduced and eliminated via biological methods because it is often a deterrent for biological treatment (6).

Reverse osmosis process that requires the use of membranes has the high cost of maintenance and replacement. Adsorption is one of the important processes in this area. Adsorption is the easiest and quickest process with no sludge as well as efficient alternative and most cost-effective for the removal of phenol (26, 32-34). To date, different materials such as activated carbon, silica and activated alumina (35), as absorbent have been used in the absorption process.

However, various problems including high cost, activation, and restoration of absorbent that are significant in economic terms (36), have prompted researchers to use the novel absorbents in view of the low cost and availability of materials, such as agricultural residues that are used widely as an absorbent for the removal of phenol (26). Due to the high level of lands under cultivation (4,956 hectares) and crop production (145,539 tons) and production of leaf wastes (427,534 tons) in Sistan and Baluchistan province, Iran, in this study we examined the efficacy of banana leaf ash in phenol removal from aqueous solution.

Materials and Methods

Banana tree leaves used in the experiments, which are known as agricultural wastes, were prepared from processing stage and after washing with distilled water were dried at 100°C for two hours to remove impurities such as sand, gravel, other leaves and color substances and solutions. Dried materials were burned at 700°C for two hours, and then were crushed in a porcelain mortar and sorted by sieves (60- 200 mesh).

The resulting absorbent powder was stored in sealed container until use (37). No chemical composition was added and no physical treatment was carried out on absorbent before the absorption process.

2-1- Preparation of Phenol Solution

Solid phenol (Merck, Germany) with a purity of 99.9% and the molecular mass of 94.11

was applied for the preparation of stock contaminated with phenol (4); 1000mg of this phenol was weighed and moved into the volumetric flask (1000ml), and brought to volume with distilled water while mixing. Next, 2ml of 1N sulfuric acid was mixed; the solution remains stable for 28 days at refrigerator temperature (4°C or lower) (38).

All tests were assessed using distilled water mixed by a certain concentration of phenol at laboratory temperature. The variables were the concentration of phenol (1, 5, 10, 15, 20 and 50 mg/l), pH (3, 5, 7, 9, 11 and 13), absorbent content (0.1, 0.2, 0.3, 0.4 and 0.5 mg/l), equilibrium adsorption time (15, 30, 45, 60, 75 and 90 minutes). In the first phase, optimal pH was determined by constant values of adsorption time, phenol concentration and absorbent content.

Secondly, by having optimal pH, constant concentration of phenol, constant value of absorbent and optimal absorption time were determined. In the next steps, likewise having the optimal pH and optimal absorption time, the amount of absorbent and ultimately the optimal concentration of phenol were determined.

All experiments were carried out using 250-ml Erlenmeyer flasks on a shaker at 120 rpm; 100 ml of sample with a certain concentration of phenol was poured into each Erlenmeyer flask, and the pH was adjusted using HCL or NaOH 1%. After the end of the contact time, the samples were filtered by Whatman filter, and kept in the refrigerator in 100-ml plastic containers.

Phenol was titrated using the reagents of 4-aminoantipyrine, mono- and di-potassium hydrogen phosphate buffer, ferric thiocyanate and ammonium hydroxide solution accordance with the procedures outlined in Section D5530, Chapter 5-47 of standard method book.

Finally, the absorption rate was read by a spectrophotometer at a wavelength of 500nm, and then remaining concentration of phenol was determined via absorption calibration curve plotted for phenol in laboratory of the device (38). The amount of

adsorbed phenol, qe (mg/g), was determined using the following equation (1):

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

Where, Ce and Co are initial and phenol equilibrium concentrations, respectively, in the liquid phase (mg/L); V is the volume of solution (L), and M is the used absorbent amount (g).

Phenol removal rate was calculated using the following equation (2):

$$\% = \frac{(C_0 - C_f)}{C_0} . 100$$

Where, C_O and C_F are, respectively, the initial and final concentrations of phenol after absorption (39). Adsorption isotherms show the distribution of molecules adsorbed in the liquid and solid phases when achieving balance.

The most common adsorption isotherm equations include Lungmuir, Freundlich and BET models. Compliance of each model with the curve associated with each balance and the correlation coefficient (R^2) were determined based on the experimental results.

Langmuir isotherm model is based on scientific assumptions. Foremost among these assumptions is that adsorbate (atoms, molecules or ions) are attached to the same certain sites on the surface of absorbent to establish monolayer adsorption process, presented by the following equation (3) (40, 41):

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

Where, q_e is the amount of phenol adsorbed per given amount of used absorbent of Ce (mg/g), Ce is solution equilibrium concentration (mg/L), and q_m is maximum amount of phenol required for the formation of two layers (mg/g). At the same time, Langmuir equation can be plotted linearly, and Langmuir adsorption constants (K_L) and

maximum absorption capacity from the absorbent (q_m) can become linear as below. The values of q_m and K_L can be achieved with charting 1/q vs. 1/Ce.
Equation (4):

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

Desirability of absorption process in the Langmuir isotherm can be determined using the values of the factor without R_L dimension, so that $R_L > 1$: undesirable absorption, R_L 1: linear absorption, $R_L = 0$: irreversible absorption, and $1 < RL > 0$: optimal absorption (42).
Equation (5):

$$R_L = 1/(1 + K_L C_0)$$

Freundlich isotherm is a merely empirical model, which is described on the basis of adsorption on the surface of absorbent in the heterogeneous form by the following equation (6):

$$q_e = K_f C_e^{\frac{1}{n}}$$

Where, kf and 1/n are Freundlich adsorption constants related to capacity and intensity of absorption. Freundlich equilibrium constants are obtained by charting the log qe vs. Log Ce based on empirical data of y-intercept of resulting curve as Kf as and the slope of the line as 1/n. At the same time, Freundlich equation can be in the form of log-linear to determine Freundlich adsorption constants as following (40, 41):
Equation (7):

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

At the end, the results of the absorption tests were presented in the form of graphs with the help of Excel software. According to two repetitions of all the tests, the values were reported as mean. In addition, linear regression statistical test was used to determine the adsorption isotherm equations.

Results and Discussion

3-1- The Effect of pH on Phenol Removal

The adsorption of phenol from aqueous solution completely depends on the pH of the solution, because the pH affects the electrical charge on the surface of the absorbent and changes the degree of phenol ionization. The effect of pH on the adsorption process is shown in Figure 1, which the amount of phenol absorbed decreases by increasing pH. The optimal pH was four for maximum removal (89.59%).

The change in the pH affects the adsorption process during the disintegration and fragmentation of related groups in the active surfaces of absorbent. As a result, this leads to a change in the absorption reaction kinetics and equilibrium properties between the absorbent and adsorbates, as well as phenol adsorption process decreases with increasing initial pH. Phenol is a weak acid, which the amount of its absorption at high pH is a loser in competition with acidic medium OH^- and so decreases, because positive surfaces of absorbent will not be willing to absorb of these phenolic ions due to electrostatic disposal.

This happens probably due to increased adsorption of $C_6H_5O^-$ to positively charged surface of absorbent; since, when the absorption rate is increased, phenol will be winner in competition with OH^- from water to neutralize the weak H^+ resulting from phenol for absorbing into absorbent, and OH^- increases in pH solution (43, 44). Srivastava et al. in 2006 evaluated the removal of phenol by bagasse ash and activated carbon, which the optimal conditions for the removal of phenol were pH about five, absorbent dose of 10 g/l, equilibrium time approximately five hours and the reaction of phenol removal of second grade (45).
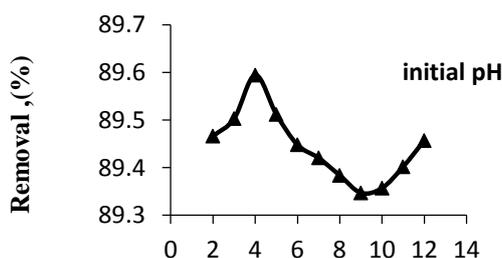

Fig 1:The effect of pH on phenol removal by the banana leaf ash (phenol concentration: 50 mg/l; ash content: 0.5 g/l; contact time: 60 minutes)

3-2- The effect of Absorbent Amount on Phenol Removal

The amount of absorbent (0.1-1g/l) for absorption testing at a constant pH of 4, initial phenol concentration of 50mg/l and laboratory temperature of 23±23°C for 60 minutes were used to determine the effect of absorbent dosage on the adsorption process (see Figure 2).

Phenol removal efficiency elevated with increasing initial amount of absorbent. The highest removal efficiency for the banana leaf ash at an absorbent dose of 0.2 g/l ash was obtained 88.98 percent. This result can be interpreted based on the fact that the remaining absorption sites were as unsaturation status during the absorption process.

However, the number of sites available for adsorption rises with increasing doses of absorbent. The maximum absorption was achieved by adding a certain dose of absorbent; thus, the amount of pollutants remained stable in the solution (46).

In a study, almond and walnut shell carbon and activated carbon were used in adsorption of phenol from contaminated water. By increasing the amount of absorbent from 0.25 to 1 g per 50 ml of activated carbon with the maximum absorption efficiency equal to 99.87% had the highest phenol removal, the almond and walnut shell carbon showed absorption efficiency of 91.36% and 87.17%, respectively.

The results of this study similar to the present experiment, phenol removal efficiency with initial concentration of 50mg/l increased from 98.91% to 98.99% by increasing the amount of absorbent from 2 grams to 11 grams per liter (44).

Liana Alvares Rodrigues et al. in 2011 conducted an in vitro study to remove phenol from aqueous solution by activated carbon produced from avocado seeds. They showed that the optimum doses of absorbent to absorb phenol was 0.1g (47).
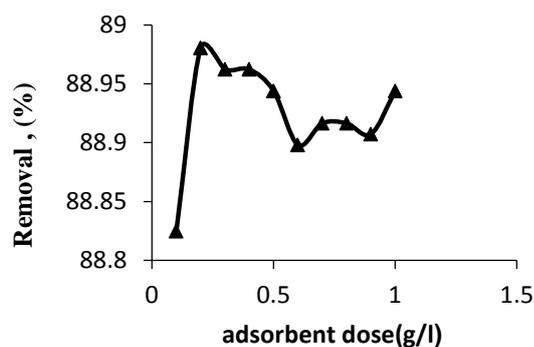
Fig 2: The effect of absorbent level for the removal of phenol by the banana leaf ash (phenol concentration: 50 mg/l; contact time: 60 minutes; pH: 4)
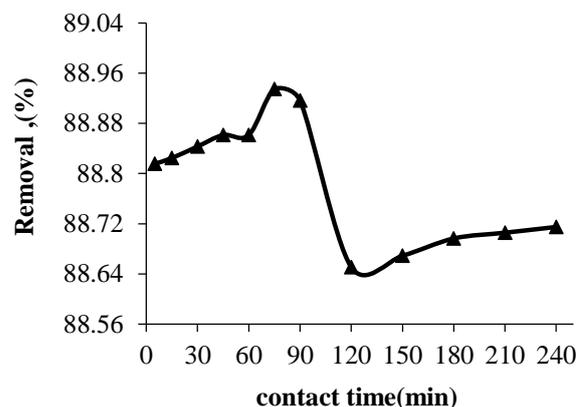

Fig 3: The effect of contact time for the removal of phenol by the banana leaf ash (phenol concentration: 50 mg/l; ash content: 0.2 g/l; pH: 5)

3-3- The Effect of Contact Time on Phenol Removal

The amount of absorbent (0.2g/l) for absorption testing at an optimal pH of 4, initial phenol concentration of 50mg/l and laboratory temperature of 23 ± 23°C for contact time (5- 240 min) were used to determine the effect of contact time on the adsorption process. Based on the results presented in Figure 3, phenol removal efficiency enhanced with increasing the contact time. The removal efficiency was maximum (88.93%) at the beginning of the process of removing up to 75 minutes, and then had a decreasing trend (from 75 to 120 minutes, and from 120 minutes to 240 minutes).

This phenomenon is due to the fact that at the beginning and the early stages of absorption, a large number of surface sites are empty for absorption; but over time, the superficial sites remained empty for the absorption of pollutants encountered a problem. That it would be due to deterrent forces among adsorbate molecules on the surface of a solid absorbent and liquid mass (48).

The results of a similar study entitled adsorption of phenol from wastewater with fibers of cylindrical sponge loofa conducted by Cherifi in 2009 showed that phenol removal was a endothermic process and phenol adsorption reached to balance after 50 minutes. The initial phenol concentration, temperature, whiteness and granularity of plants significantly influenced the absorption capacity (49).

3-4- The Effect of Initial Phenol Concentration on Removal Efficiency

According to the results related to the effect of initial phenol concentrations (Figure 4), it was observed that the absorption efficiency decreases with increasing concentrations of phenol. It seems that the absorption capacity of absorbent rises with increasing concentrations of phenol. This may be a result of increasing the force of mass transfer, and thus improving the absorption capacity.

Thus, the flow rate of phenol molecules rises from the solution toward fluid layer surrounding absorbent and ultimately toward the surface of absorbent particles (50, 51). It seems that the removal rate decreases with increasing concentrations of phenol.
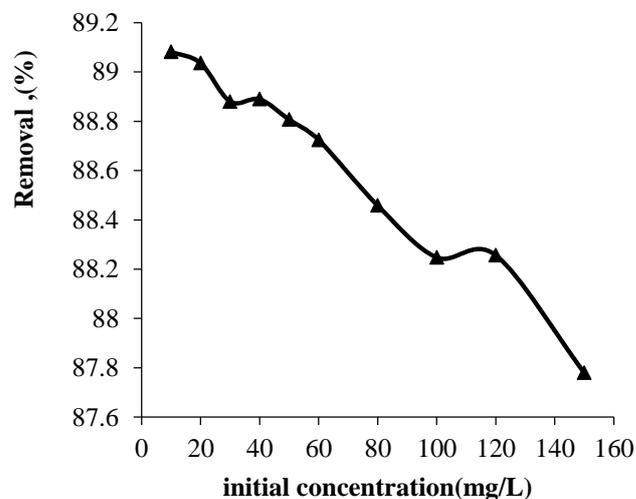

Fig 4: The effect of initial phenol concentration for the removal of phenol by the banana leaf ash (contact time: 60 minutes; ash content: 0.2 g/l; pH: 4)

3-5- Adsorption Isotherms

Figures 5 and 6 show the equilibrium isotherms for the phenol adsorption on the banana leaf ash and the equilibrium adsorption data analysis using Langmuir and Freundlich adsorption isotherms. Given the amount of regression (R^2) for each isotherm, Freundlich model had the highest value and was the best model in the phenol adsorption by the study absorbent.

Daraee, Manshoori and Yazdanbakhsh (2010) conducted a research regarding the phenol removal using ostrich feathers ash and determined that removal efficiency decreases with increasing pH, and the highest removal was found about 65% at pH=3, and the absorbent content of 2g/l, the contact time of 8 hours and the phenol concentration of 15mg/l. Also, the maximum adsorption rate was obtained at 30°C and the absorbent concentration of 0.7g/l as well as the correlation coefficients in the Langmuir and Freundlich isotherms were 0.956 and 0.989, respectively (11). coefficients in the Langmuir and Freundlich isotherms were 0.956 and 0.989, respectively (11).
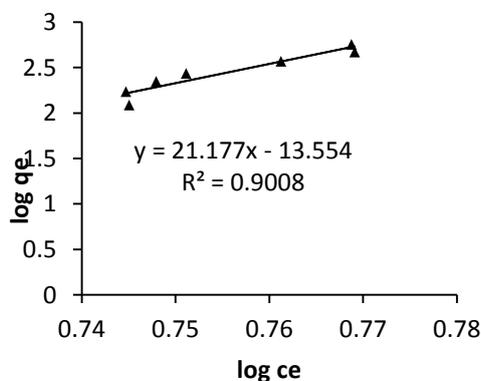

$y = 21.177x - 13.554$
$R^2 = 0.9008$

Fig 5: Freundlich adsorption isotherm for phenol adsorption by the banana leaf ash

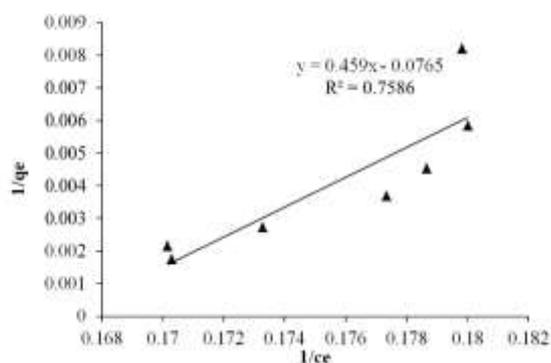$y = 0.459x - 0.0765$
$R^2 = 0.7586$

Fig 6: Langmuir adsorption isotherm for phenol adsorption by the banana leaf ash

Conclusion

Maximum efficiency for the adsorption of phenol from contaminated water for absorbent achieved from banana leaf ash according to the results of the present study was found at the absorbent concentration of 0.2 g/l, relatively modest initial pH and 4 in the optimal condition and contact time of 75 minutes for mixing samples and a concentration of 10 mg/l. The Freundlich isotherm model had the highest rate, so was considered as the best model in the phenol adsorption by study absorbent (R^2 0.900).

References

1. Bazrafshan E, Biglari H, Mahvi AH. Phenol removal by electrocoagulation process from aqueous solutions. Fresenius Environmental Bulletin. 2012;21(2):364-71.

2. Saeedi M, Investigation of contaminated water using activated carbon and carbon adsorption of phenol peel almonds and walnuts Journal of Environmental Science and Technology (JEST)2012;10(3):218-231.

3. 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 Oct 15;174(1):49-57.

4. Biglari H, Saeidi M, Alipour V, Rahdar S, Sohrabi Y, Khaksefidi R, et al. Review on hydrochemical and health effects of it in Sistan and Baluchistan groundwater's, Iran. International Journal of Pharmacy and Technology. 2016;8(3):17900-20.

5. Jamshidi N,Torabian A, Azimi AA, Nabi Bidhendi GR, Jafarzadeh MT. Investigation of Phenol Removal in Aqueous Solutions Using Advanced Photochemical Oxidation (APO). J. of Water and Wastewater. 2009;24(4):25-29.

6. Lua AC, Jia Q. Adsorption of phenol by oil–palm-shell activated carbons in a fixed bed. Chemical Engineering Journal. 2009 Aug 1;150(2):455-61.

7. Srihari V, Das A. Comparative studies on adsorptive removal of phenol by three agro-based carbons: equilibrium and isotherm studies. Ecotoxicology and environmental safety. 2008 Sep 30;71(1):274-83.

8. Liu QS, Zheng T, Wang P, Jiang JP, Li N. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chemical Engineering Journal. 2010 Mar 1;157(2):348-56.

9. Hameed BH, Rahman AA. Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. Journal of Hazardous Materials. 2008 Dec 30;160(2):576-81.

10. Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: a short review of recent developments. Journal of Hazardous Materials. 2008 Dec 30;160(2):265-88.

11. Daraei H, Manshouri M, Yazdanbakhsh AR. Removal of phenol from aqueous solution using ostrich feathers ash. Mazand Univ Med Sci. 2010 Sep 15;20(79):81-7.

12. 12-Özkaya B. Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models. Journal of hazardous materials. 2006 Feb 28;129(1):158-63.

13. Manojlovic D, Ostojic DR, Obradovic BM, Kuraica MM, Krsmanovic VD, Puric J. Removal of phenol and chlorophenols from water by new ozone generator. Desalination. 2007 Jul 15;213(1):116-22.

14. Biglari H, Saeidi M, Alipour V, Rahdar S, Sohrabi Y, Khaksefidi R, et al. Prospect of disinfection byproducts in water resources of Zabol. International Journal of Pharmacy and Technology. 2016;8(3):17856-65.

15. Vasiliadou IA, Tziotzios G, Vayenas DV. A kinetic study of combined aerobic biological phenol and nitrate removal in batch suspended growth cultures. International Biodeterioration & Biodegradation. 2008 Apr 30;61(3):261-71.

16. Abdelwahab O, Amin NK, El-Ashtoukhy EZ. Electrochemical removal of phenol from oil refinery wastewater. Journal of hazardous materials. 2009 Apr 30;163(2):711-6.

17. Asgari G, Sidmohammadi A, Ebrahimi A, Gholami Z, Hosseinzadeh E. Study on phenol removing by using modified zolite (Clinoptilolite) with FeCl3 from aqueous solutions. J Health Syst Res 2010;89:848-57. (Persian)

18. Azevedo EB, de Aquino Neto FR, Dezotti M. Lumped kinetics and acute toxicity of intermediates in the ozonation of phenol in saline media. Journal of hazardous materials. 2006 Feb 6;128(2):182-91.

19. Andrews JF. A mathematical model for the continuous culture of microorganisms utilizing inhibitory substrates. Biotechnology and Bioengineering. 1968 Nov 1;10(6):707-23.

20. Tchobanoglous G, Burton FL, Stensel HD.Wastewater engineering treatment and reuse

21. Metcalf and Eddy, McGraw-Hill, Inc, FourthEdition, 2003;360-389.

22. US Department of Health and Human Services. Agency for Toxic Substances and Disease Registry. Toxicological Profile for Asbestos. Update. Agency for Toxic Substances and Disease Registry. 1999 Jun.

23. 22-Din AT, Hameed BH, Ahmad AL. Batch adsorption of phenol onto physiochemical-activated coconut shell. Journal of Hazardous Materials. 2009 Jan 30;161(2):1522-9.

24. Mukherjee S, Kumar S, Misra AK, Fan M. Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. Chemical Engineering Journal. 2007 May 1;129(1):133-42.

25. Lin SH, Juang RS. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. Journal of environmental management. 2009 Mar 31;90(3):1336-49.

26. Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: a short review of recent developments. Journal of Hazardous Materials. 2008 Dec 30;160(2):265-88.

27. Dursun G, Cicek H, Dursun AY. Adsorption of phenol from aqueous solution by using carbonised beet pulp. Journal of hazardous materials. 2005 Oct 17;125(1):175-82.

28. Tor A, Cengeloglu Y, Aydin ME, Ersoz M. Removal of phenol from aqueous phase by using neutralized red mud. Journal of colloid and interface science. 2006 Aug 15;300(2):498-503.

29. Zazo JA, Casas JA, Mohedano AF, Rodriguez JJ. Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst. Applied Catalysis B: Environmental. 2006 Jun 6;65(3):261-8.

30. Quintanilla A, Casas JA, Mohedano AF, Rodríguez JJ. Reaction pathway of the catalytic wet air oxidation of phenol with a Fe/activated carbon catalyst. Applied Catalysis B: Environmental. 2006 Oct 5;67(3):206-16.

31. Carbajo M, Beltran FJ, Medina F, Gimeno O,Rivas FJ. Catalytic ozonation of phenolic compounds: the case of gallic acid, Appl Catal B-Environ. 2006; 67: 177–86.

32. Caetano M, Valderrama C, Farran A, Cortina JL. Phenol removal from aqueous solution by adsorption and ion exchange mechanisms onto polymeric resins. Journal of Colloid and Interface Science. 2009 Oct 15;338(2):402-9.

33. Yousef RI, El-Eswed B, Ala'a H. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies. Chemical Engineering Journal. 2011 Jul 15;171(3):1143-9.

34. El-Naas MH, Al-Zuhair S, Alhaija MA. Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon. Chemical Engineering Journal. 2010 Sep 1;162(3):997-1005.

35. Senturk HB, Ozdes D, Gundogdu A, Duran C, Soylak M. Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study. Journal of Hazardous Materials. 2009 Dec 15;172(1):353-62.

36. Sajjadi SA, Asgari G, Biglari H, Chavoshani A. Pentachlorophenol removal by persulfate and microwave processes coupled from aqueous

environments. Journal of Engineering and Applied Sciences. 2016;11(5):1058-64.

37. Kitis M, Karakaya E, Yigit NO, Civelekoglu G, Akcil A. Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide. Water Research. 2005 Apr 30;39(8):1652-62.

38. Bazrafshan E, Kord Mostafapour F, Heidarinezhad F.Phenol removal from aqueous solutions using Pistachio hull ash as a low cost adsorbent. Quarterly Journal of Sabzevar University of Medical Sciences, 2013;20(2) :142-153.

39. 38-Standard methods for the examination of water and wastewater 20Th , 2005 , Section 5–47 , direct method.

40. APHA. Standard Methods for the Examination of Waters and Wastewaters. 20th ed. Washington, DC: American Public Health Association (APHA); 1998.

41. 40-Hameed BH, Tan IA, Ahmad AL. Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6-trichlorophenol on coconut husk-based activated carbon. Chemical Engineering Journal. 2008 Oct 15;144(2):235-44.

42. Montazer-Rahmati MM, Rabbani P, Abdolali A, Keshtkar AR. Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae. Journal of hazardous materials. 2011 Jan 15;185(1):401-7.

43. Kakavandi B, Rezaei Kalantary R, Jonidi Jafari A, Esrafily A, Gholizadeh A, Azari A. Efficiency of powder activated carbon magnetized by Fe3O4 nanoparticles for amoxicillin removal from aqueous solutions: Equilibrium and kinetic studies of adsorption process. Iranian Journal of Health and Environment. 2014 Jul 15;7(1):21-34.

44. Mahvi A. H, Maleki, A,Eslami, A. Potential of rice husk and rice husk ash for phenol removal in aqueous system, Am. J. Appl. Sci.,2004;1(4):321-326.

45. Al-Muhtaseb SA. Adsorption and desorption equilibria of nitrogen, methane, ethane, and ethylene on date-pit activated carbon. Journal of Chemical & Engineering Data. 2009 Oct 16;55(1):313-9.

46. Srivastava VC, Swamy MM, Mall ID, Prasad B, Mishra IM. Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2006 Jan 5;272(1):89-104.

47. Bazrafshan E, Mostafapour FK, Faridi H, Farzadkia M, Sargazi S, Sohrabi A. Removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D) from aqueous environments using single-walled carbon nanotubes. Health Scope. 2013 May;2(1):39-46.

48. 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 Oct 15;174(1):49-57.

49. Cengiz S, Cavas L. Removal of methylene blue by invasive marine seaweed: Caulerpa racemosa var. cylindracea. Bioresource Technology. 2008 May 31;99(7):2357-63.

50. Cherifi H, Hanini S, Bentahar F. Adsorption of phenol from wastewater using vegetal cords as a new adsorbent. Desalination. 2009 Aug 31;244(1):177-87.

51. Mittal A. Removal of the dye, Amaranth from waste water using hen feathers as potential adsorbent. Electron. J. Environ. Agric. Food Chem. 2006;5(2):1296-305.

52. 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 Management. 2002 Aug 31;22(5):543-8.