Journal of Human, Environment and Health Promotion. 2018; 4(4): 175-179

Journal of Human, Environment and Health Promotion

Journal homepage: www.zums.ac.ir/jhehp

Adsorption of Catechol from Aqueous Solutions Using Graphene Oxide

Abdul Jalil Tazerodi [a] | **Hamideh Akbari** [b] | **Ferdos Kord Mostafapour** [b]*

[a] *Department of Environmental Health, Student Research Committee, Zahedan University of Medical Sciences, Zahedan, Iran.*
[b] *Department of Environmental Health, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran.*

***Corresponding author:** Ferdos Kord Mostafapour
Department of Environmental Health, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran. Postal code: 9816743463.
E-mail address: ferdosm66@gmail.com

ARTICLE INFO

Article type:
Original article

Article history:
Received October 23, 2018
Revised November 24, 2018
Accepted December 4, 2018

DOI: 10.29252/jhehp.4.4.6

Keywords:
Catechol
Isotherm
Hazardous compounds
Graphene oxide

ABSTRACT

Background: Catechol is considered as apriority pollutant, since it is harmful to organisms even at low concentrations, and has been classified as hazardous pollutants. The aim of this study was to investigate catechol adsorption by graphene oxide of aqueous solution.

Methods: This study was an experimental-laboratory research. The batch adsorption system was utilized to evaluate the Catechol removal efficiency under different amount of effective parameters including contact time, adsorbent dosages and Catechol concentration. The experimental data were analyzed by the Langmuir, Freundlich, Temkin isotherm models.

Results: R^2 value of Langmuir isotherm model is higher than other models and maximum monolayer coverage (q_{max}) was calculated to be 79.08 mg/g and the separation factor indicating a favorable sorption experiment is 0.242. Also from Freundlich isotherm model, the intensities of adsorption (n) that indicated favorable sorption is 3.324. The maximum removal efficacy (94.7%) was at concentration 100 mg/L, pH 7, adsorbent dosage 1200 mg/L and contact time 75 min.

Conclusion: According to the results, the adsorption process using graphene oxide was effective in the removal of catechol. Therefore, the use of this cost-effective agent is recommended as a proper alternative for the removal of catechol from aqueous solutions.

1. Introduction

Removal of hazardous compounds from industrial effluents is a growing need in the modern era [1, 2]. Phenol and substituted phenol are important organic intermediates for industrial and agricultural products [3, 4]. For instance, aromatic hydroxyl compounds, such as catechol, are widely applied as industrial solvents [5]. Catechol, pyrocatechol, and o-hydroxyphenol are often used as topical antiseptics, as well as in photography, fur dying, leather tanning, antifungal preservation of potato seed pieces, and polymerization inhibitors. Furthermore, catechol is used as a chemical intermediate and an antioxidant in numerous industries.

Chemical laboratories employ catechol for the detection and determination of various ions. Therefore, catechol frequently contaminates the wastewaters generated by rubber, chemical, photographic, pharmaceutical, cosmetic, and oil industries [6, 7]. Catechol causes significant irritability to the eyes, skin, and respiratory tract, while it has proven to cause DNA damage, vascular collapse, coma, and death [8]. For public health and environmental protection against the hazards associated with catechol, catechol-bearing aqueous waste must be treated using efficient, cost-effective, and environmentally benign techniques before it is discharged [9, 10].

To cite: Tazerodi AJ, Akbari H, Kord Mostafapour F. Adsorption of Catechol from Aqueous Solutions Using Graphene Oxide. *J Hum Environ Health Promot*. 2018; 4(4): 175-9.

According to a literature review in this regard, most of the investigations regarding the removal of phenolic compounds from wastewater have been focused on physical, chemical, and biological processes [11, 12]. Although chemical processes such as photocatalysis, Fenton, photo-Fenton and ozonation are highly efficient, they are among the costly methods used for the mineralization of catechol [13]. In addition, these processes are often incomplete and generate by-products, which contribute to severe health risks and environmental hazards [14].

Traditionally, some of the techniques that are widely used for the removal of phenols and the related organic substances include biological treatment, activated carbon adsorption, reverse osmosis, ion exchange, and solvent extraction [15]. Among these methods, adsorption on activated carbon remains a highly applicable technique [16]. Numerous researchers have claimed that activated carbon is an effective adsorbent for organic compounds, especially phenolic compounds, owing to its high surface area per unit mass, as well as the high adsorption capacity for phenolic compounds. However, the high initial costs and need for costly regeneration systems make this method less economical as an adsorbent [17, 18].

Several attempts have been recorded in laboratories in order to replace activated carbon by other adsorbents, such as graphene oxide [19]. Graphene oxide is an important derivative of graphene, which has been extensively studied. Some of the main advantages of graphene oxide (GO) are the sufficient quantity of oxygenous functional groups (e.g., epoxide, hydroxyl, and carboxyl groups), large specific surface area, and high water solubility, which makes it an optimal adsorbent [20].

The present study aimed to investigate the removal of catechol from aqueous solutions using graphene oxide and assess the effects of the initial catechol concentration, contact time, and adsorbent dosage on the static adsorption of the catechol/GO system. In addition, a model of the adsorption isotherms was proposed by fitting the parameters of the Langmuir, Freundlich, and Temkin models.

2. Materials and Methods

Catechol, also known as pyrocatechol ($C_6H_4^{-1}$, 2 $(OH)_2$), is a phenolic compound, which was used as a sorbate in this study. Catechol C. I. 120809 with the molecular weight of 110.11 was purchased from Merck, Germany. A stock solution (1,000 mg/l) was prepared, and the working solutions were prepared by diluting the stock solution by distilled water as required. Other chemicals (HCl and NaOH) were of an analytical grade and supplied by Merck as well.

The efficiency of the adsorbent was evaluated by conducting laboratory batch mode studies. Specific amounts of the adsorbent were shaken in 100 milliliters of an aqueous solution containing various concentrations of catechol at different time intervals, natural pH, and temperatures. After the pre-determined intervals, the adsorbent was removed by centrifugation at 2,000 rpm (Centric 400R model), and the supernatant was analyzed for the residual concentration of catechol spectrophotometrically at the wavelength of 280 nanometers [8]. Moreover, the variations in the adsorbent dosage, contact time, and initial concentration of catechol were assessed. Finally, the removal rate of catechol was calculated based on Equation 1, as follows [14]:

$$\%\ R = \left[\frac{C_0 - C_e}{C_e}\right] \times 100 \tag{1}$$

The adsorption capacity (q_e) for the GO adsorbent (mg/g) was determined based on Equation 2, as follows [15]:

$$q_e = \left[\frac{C_0 - C_e}{m}\right] V \tag{2}$$

Where C_0 is the initial concentration of catechol (mg/l), C_e represents the equilibrium concentrations of catechol in the solution (mg/l), V shows the volume of the solution (l), and m is the weight of the GO adsorbent (g).

3. Results and Discussion

3.1. Effect of GO Dosage

GO dosage in a solution remarkably affects the adsorption process. As is shown in Figure 1, the effect of the GO dosage was investigated at the catechol concentration of 100 mg/, pH of 7, and contact time of 75 minutes. The GO adsorbent exhibited the maximum adsorption of 348.1 mg/g at the dosage of 1,200 mg/l. With the constant initial concentration of catechol, the adsorption capacity decreased with the increased dosage of the adsorbent. On the other hand, the adsorbent could be used feasibly at low dosages, which was due to the fact that the binding sites and surface area of GO could be used effectively at low dosages, and the increased ratio of catechol to adsorbent decreased increasing the dosage [21].

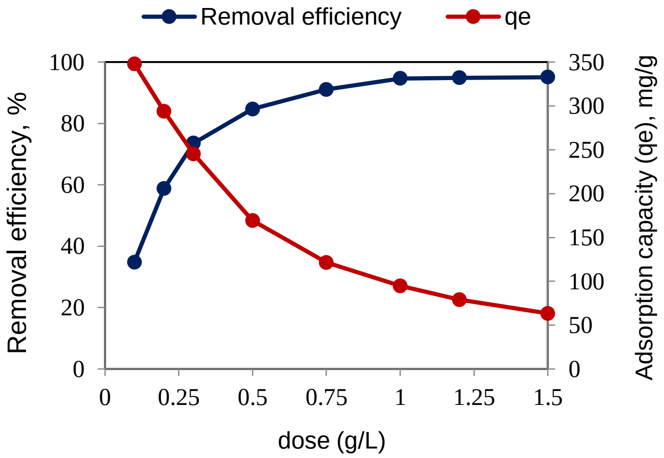

Figure 1: Effect of Adsorbent Dosage on Efficiency of Catechol Adsorption (C_0: 100 mg/l, temperature: 25 °C, pH: 7, Contact time: 75 minutes)

3.2. Effect of Contact Time

The effect of contact time was assessed at the catechol concentration of 100 mg/l. Figure 2 depicts the correlation between the contact time and catechol removal efficiency. The observations revealed that the removal rate of catechol was higher with the increased contact time; the removal occurred rapidly in the beginning and remained nearly constant after 60 minutes. This could be due to the large number of the available vacant surface sites is for adsorption during the initial stage and with time [22]. After a while, the repulsive forces between the solute molecules on the solid and liquid phases caused difficulty for the solute molecules to occupy the remaining vacant surface sites [23, 24].

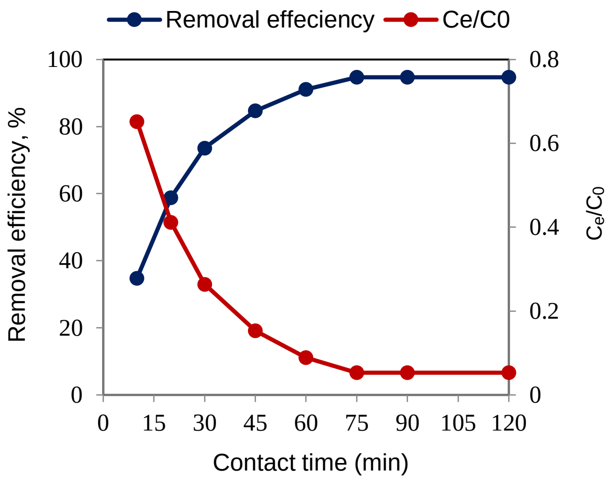

Figure 2: Effect of Contact Time on Efficiency of Catechol Adsorption (C_0: 100 mg/l, temperature: 25 °C, pH: 7, adsorbent dosage: 1,200 mg/l)

3.3. Adsorption Isotherm

Isotherms are considered to be the important, basic requirements for the analysis of adsorption systems, and more isotherms are required for design purposes. In the present study, a series of experiments were performed to evaluate the sorption of GO, which was further verified using the Langmuir, Freundlich, and Temkin isotherms.

Based on the Langmuir adsorption, biosorption onto the adsorbent surface is homogeneous in nature. According to the Langmuir isotherm, the sorbent surface occurred as monolayer biosorption on a homogeneous number of the exchanging sites. This phenomenon could describe the uniform sorption energy on the biosorbent surface. The non-linear Langmuir isotherm equation has been presented in Equation 3, as follows [25]:

$$q_e = \frac{q_m C_0}{1+bC_0} \qquad (3)$$

Equation 3 could be linearized as Equation 4, as follows [26]:

$$\frac{Ce}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (4)$$

where q_e and q_m (mg/g) show the equilibrium capacity of sorption and maximum adsorption capacity, respectively, C_e (mg/l) represents the equilibrium concentration of catechol, and b (l/mg) is the constant of the affinity and energy binding sites.

The essential features of the Langmuir isotherm may be expressed in terms of the equilibrium parameter R_L, which is a dimensionless constant referred to as the 'separation factor' or equilibrium parameter [27]:

$$R_L = \frac{1}{1+bc_0} \qquad (5)$$

The R_L value indicates the adsorption nature to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich adsorption isotherm (Equations 6 and 7) is commonly used to describe the adsorption characteristics of heterogeneous surfaces, as well as multilayer sorption. The data often fit the empirical equation proposed by Freundlich [28].

$$qe = K_F\, C_e^{1/n} \qquad (6)$$

This equation could be linearized into a logarithmic form for data fitting and parameter evaluation, as follows [29]:

$$\text{Log } q_e = \frac{1}{n} \log C_e + \log K_F \qquad (7)$$

where K_F is the Freundlich isotherm constant ((mg/g) [l/mg] 1/n), n shows the adsorption intensity, C_e represents the equilibrium concentration of the adsorbate (mg/l), and qe is the amount of the adsorbed catechol per gram of the adsorbent at the equilibrium (mg/g). It is notable that the K_F constant is an approximate indicator of the adsorption capacity, while 1/n is a function of the adsorption strength in the adsorption process; as such, lower 1/n is associated with the higher expected heterogeneity.

In the current research, Temkin model was tested for equilibrium description at room temperature, and the model is presented in Equation 8, as follows [30].

$$qe = B \text{ Ln } A + B \text{ Ln } Ce \qquad B = \frac{RT}{b} \qquad (8)$$

where B is the Temkin constant related to the sorption heat (J/mol), K_T shows the Temkin isotherm constant (l/g), R represents the gas constant (8.314 J/mol K), b is the Temkin isotherm constant, and T is the temperature (K) [30].

The linear regression equations and determination coefficient (R^2) generated for the Langmuir isotherm are depicted in Figure 3. The R_L value (separation factor) was estimated at 0.242, and the R^2 value was determined to be 0.989, indicating the favorable equilibrium sorption and proved that the sorption data fitted well to the Langmuir isotherm model as the confirmation of the chemisorption process. These findings were also confirmed by the values of the Langmuir constant (K_L) and maximum monolayer coverage capacity (q_{max}), which were calculated to be 0.372 and 79.08 mg/g, respectively.

Figure 4 shows the isotherm equation used to analyze the equilibrium isotherms of the catechol ions, which provided the linear plots, linear regression equations, and regression coefficients (R^2) for the Freundlich model ($R^2 = 0.868$). Based on the data calculated by the Freundlich equation, n and K_F were estimated at 3.324 and 0.741, respectively.

Based on the Temkin plot (Figure 5), KT was estimated at 0.546 l/g, b was determined to be 146.85 l/g, R^2 was calculated to be 0.811, and B was estimated at 16.87 J/mol. These data indicated that sorption was a physical process (B < 20 KJ/mol). Therefore, it could be concluded that the Temkin equation did not represent a better fit to the experimental data.

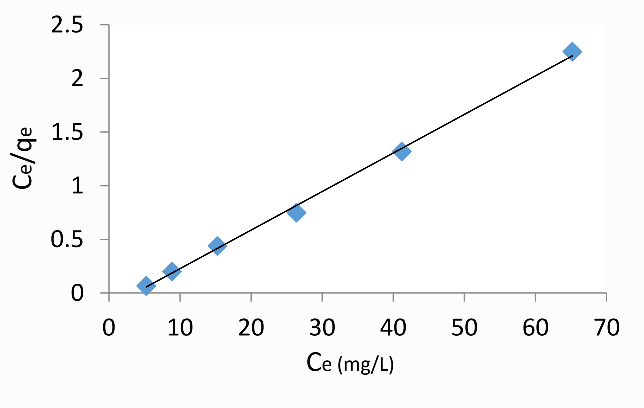

Figure 3: Langmuir plots for adsorption of catechol onto GO

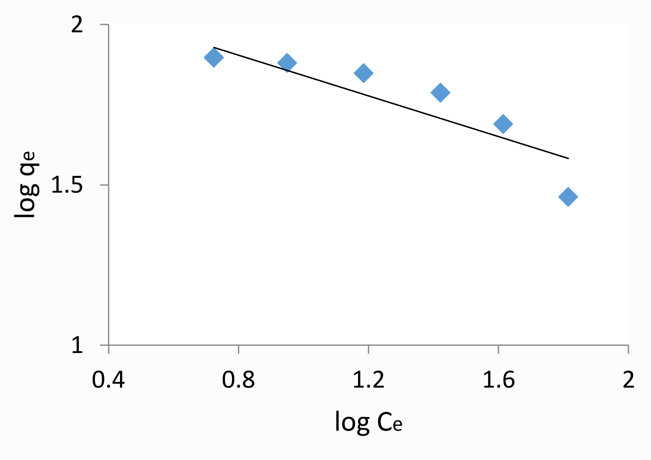

Figure 4: Freundlich plots for adsorption of catechol onto GO

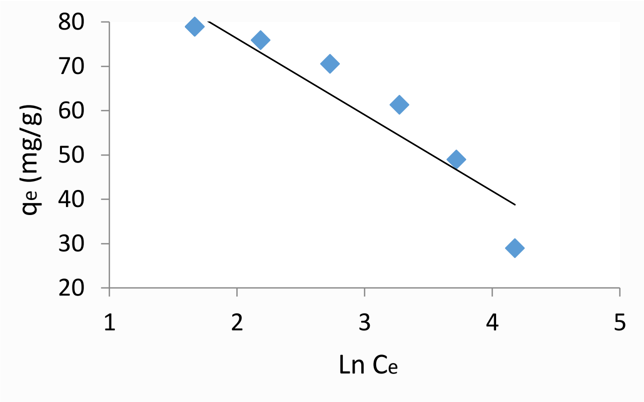

Figure 5: Temkin plots for adsorption of catechol onto GO

Table 1: Comparison of maximum adsorption capacities of catechol by various adsorbents

Adsorbent	qe (mg/g)	Ref	Adsorbent	qe (mg/g)	Ref
dolomite	51.8	[1]	Organophilic-bentonite	89.3	[8]
Chitosan	41.9	[4]	Azolla filiculoides	29.6	[15]
Bentonite	38.6	[4]	Lemna minor	21.4	[9]
Activated carbon	56.8	[6]	GO	79.08	This study

4. Conclusion

This study examined the application of GO for removal of catechol from aquatic systems. The adsorption of catechol from aqueous solution on the GO was investigated with variations in contact time, initial catechol concentration and adsorbent dosage. The results showed that the adsorption of catechol onto GO increased within 75 min and reached equilibrium gradually and removal percentage was 94.7 at catechol concentration of 100 mg/L and adsorbent dose of 1200 mg/L. The adsorption behavior of catechol onto GO was best described by the Langmuir isotherm. The results also indicated that the type of adsorption involved in this study is physiosorption (physical sorption). The results also revealed that GO is a promising adsorbent for removal of catechol from industrial wastewater.

Authors' Contributions

A.J.T., designed the interviews forms for all sectors with F.K.M., collaboration and conducted the interview. H.A., helped and analyzed the statistical data. All authors revised and approved the final manuscript.

Conflict of Interest

The authors affirm that there is no conflicts of interest that may have influenced the preparation of this manuscript.

Acknowledgments

The authors are grateful to the Zahedan University of Medical Sciences for the financial support of this study (Project No. 8165).

References

1. Khalfa A, Mellouk S, Marouf-Khelifa K, Khelifa A. Removal of Catechol from Water by Modified Dolomite: Performance, Spectroscopy, and Mechanism. *Water Sci Technol*. 2018; 77(7): 1920-30.

2. Cohen SH, Belinky PA, Hadar Y, Carlos G. Dosoretz D. Characterization of Catechol Derivative Removal by Lignin Peroxidase in Aqueous Mixture. *Bioresour Technol*. 2009; 100: 2247-53.

3. Schweigert N, Zehnder AJB, Eggen RL. Chemical Properties of Catechols and Their Molecular Modes of Toxic Action in Cells, from Microorganisms to Mammals. *Environ. Microbiol*. 2001; 3: 81-91.

4. Suresh S, Srivastava VC, Mishra IM. Adsorption of Catechol, Resorcinol, Hydroquinone, and Their Derivatives: A Review. *Int J Energy Environ Eng*. 2012; 32(3): 1-19.

5. Balarak D, Joghataei A. Biosorption of Phenol Using Dried Rice Husk Biomass: Kinetic and Equilibrium Studies. *Der Pharma Chemica*. 2016; 8(6): 96-103.

6. Kumar A, Kumar S, Kumar S. Adsorption of Resorcinol and Catechol on Activated Carbon: Equilibrium and Kinetics. *Carbon*. 2003; 41: 3015-25.

7. Namasivayam C, Sumithra S. Adsorptive Removal of Catechol on Waste Fe(III)/Cr(III) Hydroxide: Equilibrium and Kinetics Study. *Ind Eng Chem Res*. 2004; 43(23): 7581-87.

8. Shakir K, Ghoneimy HF, Elkafrawy AF, Beheir SG, Refaat M. Removal of Catechol from Aqueous Solutions by Adsorption onto Organophilic-Bentonite. *J Hazard Mater*. 2008; 150: 765-73.

9. Balarak D , Bazrafshan E, Mahdavi Y. Biosorption of Pyrocatechol Using Dried Lemna minor: Kinetic and Equilibrium Studies. *Zanko J Med Sci*. 2015; 16 (50): 13-26.

10. Zhou Z, Ping L, Jun L. Application of Natural Biosorbent and Modified Peat for Bisphenol a Removal from Aqueous Solutions. *Carbohydr Polym*. 2012; 88(2): 502-8.

11. Senturk H, Ozdesa D, Gundogdua A, Durana C, Oylak M. Removal of Phenol from Aqueous Solutions by Adsorption onto Organo-Modified Tirebolu Bentonite: Equilibrium, Kinetic and Thermodynamic Study. *Hazard Mater*. 2009; 172: 353-62.

12. Mandal A, Ojha K, De AK. Removal of Catechol from Aqueous Solution by Advanced Photo-oxidation Process. *Chem Eng J* . 2004; 102(2): 203-8.

13. Sadler A, Subrahmanyam VV, Ross D. Oxidation of Catechol by Horseradish Peroxidase and Human Leukocyte Peroxidase: Reactions of O-benzoquinone and Obenzosemiquinone. *Toxicol Appl Pharmacol*. 1988; 93(1): 62-71.

14. Gholizadeh A, Kermani M, Gholami M, Farzadkia M. Comparative Investigation of 2-Chlorophenol and 4-Chrorophenol Removal Using Granulated Activated Carbon and Rice Husk Ash. *Tolooe Behdasht*. 2013; 11(3): 66-78

15. Diyanati RA, Yousefi Z, Cherati JY. The Ability of Azolla and Lemna minor Biomass for Adsorption of Phenolic Compounds from Aqueous Solutions. *J Mazandaran Univ Med Sci*. 2013; 23(106): 21-8.

16. Kumar Nadavala S, Swayampakula K, Boddu VM, Abburia K. Biosorption of Phenol and Ochlorophenol from Aqueous Solutions on to Chitosan Calcium Alginate Blended Beads. *J Hazard Mater*. 2009; 162: 482-9.

17. Williams G, Seger B, Kamat PV. TiO_2–Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano*. 2008; 2: 1487-91.

18. Akhavan O, Abdolahad M, Esfandiar A, Mohatashamifar M. Photodegradation of Graphene Oxide Sheets by TiO_2 Nanoparticles after a Photocatalytic Reduction. *J Phys Chem C*. 2010; 114: 12955-9.

19. Yang ST, Chen S, Chang Y, Cao A, Liu Y. Removal of Methylene Blue from Aqueous Solution by Graphene Oxide. *J Colloid Interface Sci*. 2011; 359: 24-9.

20. Zazoulli MA, Balarak D. The Ability of Azolla and Lemna minor Biomass to Adsorption Pcresol from Aqueous Solutions: Isotherms and Kinetics. *J Health Field*. 2014; 2(1): 35-45.

21. Sui Q, Huang J, Liu Y, Chang X, Ji G, Deng S, et al. Rapid Removal of Bisphenol A on Highly Ordered Mesoporous Carbon. *J Environ Sci*. 2008; 23(2): 172- 82.

22. Qadeer R. A Study of the Adsorption of Phenol by Activated Carbon from Aqueous Solutions. *Turk J Chem*. 2002; 26: 357-61.

23. Balarak D, Mahdavi Y, Kord Mostafapour F, Joghataei A. Batch Removal of Acid Blue 292 dye by Biosorption onto Lemna minor: Equilibrium and Kinetic Studies. *J Hum Environ Health Promot*. 2016; 2(1): 9-19.

24. 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 Surf A Physicochem Eng Asp*. 2006; 272: 89-104.

25. Subramanyam B, Das A. Study of the Adsorption of Phenol by Two Soils Based on Kinetic and Isotherm Modeling Analyses. *Desalination*. 2009; 249(3): 914-21.

26. Moussavi SP, Mohammadian Fazli M. Acid Violet 17 Dye Decolorization by Multi-Walled Carbon Nanotubes from Aqueous Solution. *J Hum Environ Health Promot*. 2016; 1(2): 110-7.

27. Banat FA, Al-Bashir B, Al-Asheh S, Hayajneh O. Adsorption of Phenol by Bentonite. *Environ Pollut*. 2000; 107(3): 391-8.

28. Balarak D, Mahdavi Y, Jogatayi A. Removal of Phenolic Compounds Using Canola Stalks Waste as a new low Cost adsorbent *Int J Innov Res Sci Eng Technol*. 2015; 2(8): 735-44.

29. Baker HM, Ghanem R. Evaluation of Treated Natural Zeolite for the Removal of Ochlorophenol from Aqueous Solution. *Desalination*. 2009; 249: 1265–72.

30. Balarak D, Dashtizadeh M, Abasizade H, Baniasadi M. Isotherm and Kinetic Evaluation of Acid Blue 80 Dye Adsorption on Surfactant-Modified Bentonite. *J Hum Environ Health Promot*. 2018; 4 (2): 75-80.