

Phenol Removal from Aqueous Environment by Adsorption onto Pomegranate Peel CarbonMojtaba Afsharnia¹, Mahdi Saeidi², Amin Zarei³, Mohammad Reza Narooie⁴, Hamed Biglari⁵

¹ Ph.D. of Environmental Health, Assistant Professor, Department of Environmental Health Engineering, School of Public Health, Social Development & Health Promotion Research Center, Gonabad University of Medical Sciences, Gonabad, Iran

² M.Sc. of Environmental Health, Instructor, Department of Environmental Health Engineering, School of Public Health, Torbat Heydarieh University of Medical Sciences, Torbat Heydarieh, Iran

³ M.Sc. of Environmental Health, Senior Lecturer, Department of Environmental Health Engineering, School of Public Health, Mashhad University of Medical Science, Mashhad, Iran

⁴ M.Sc. of Environmental Health, Senior Lecturer, Department of Environmental Health Engineering, School of Public Health, Iranshar University of Medical Sciences, Iranshar, Iran

⁵ M.Sc. of Environmental Health, Senior Lecturer, Department of Environmental Health Engineering, School of Public Health, Social Development & Health Promotion Research Center, Gonabad University of Medical Science, Gonabad, Iran

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Abstract

Introduction: Phenol and its derivatives are the most common poisonous compounds which are stable in aqueous media and lead to many health issues. In this study, application of the carbon resulted from pomegranate peel is investigated in removal of phenol by adsorption method.

Methods: to perform this cross-sectional study, first, samples of phenol with concentrations of 10 to 100 mg/L were prepared for six months in 2016. Then, the impacts of parameters such as pH, adsorbent dosage, contact time, and initial concentration of phenol in adsorption process were investigated independently in Gonabad Chemistry Lab using a spectrophotometer at 505 nm as the wavelength. Furthermore, adherence of the samples to the isotherm models of Langmuir and Freundlich was determined by Excel 2016 and descriptive statistical methods were then reported.

Results: The obtained results demonstrated a maximum adsorption capacity (ash) of 148.38 mgg⁻¹ at pH 7, initial concentration of 100 mg L⁻¹, and temperature of 23 ± 2 °C. The phenol removal rate was found to correlate directly to the adsorbent dosage and contact time, and inversely to the initial concentration of phenol. In addition, the investigations showed that the adsorption of phenol on the pomegranate peel ash follows the Freundlich model well with a correlation coefficient of R² 0.9056.

Conclusion: Pomegranate peel ash could be used as an efficient and low-cost adsorbent for phenol removal from aqueous media.

Keywords: Adsorption, Aqueous solution, Pomegranate peel, Activated carbon, Freundlich, Langmuir isotherm

1. Introduction

Presence of toxic and stable compounds in the environment has led to major health and environmental problems. Phenol is one of the most common contaminants found in wastewater of industries such as resin, plastics, explosives, steel, leather, etc. The phenol released from these industries causes contamination of the environment, in particular water sources. This compound forms compounds such as chlorophenol which are classified as priority pollutants due to their certain features such as high toxicity, carcinogenicity, impact on the taste and odor, accumulative, low

Corresponding author:

Hamed Biglari, Department of Environmental Health Engineering, School of Public Health, Social Development & Health Promotion Research Center, Gonabad University of Medical Science, Gonabad, Iran.

Tel: +98.5157225027, Fax: +98.5157223814, Email: Biglari.h@gmu.ac.ir

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biodegradability potential, and many other adverse effects on human health and other living things, and has attracted the attention of many environment experts (1, 4, 5). The health effects caused by exposure to phenol can be determined by the amount of the phenol adsorbed as well as the contact time. These effects could vary from mucosal and skin irritation and burns to systemic toxicity as well as decreased blood pressure, increased heart rate and coma (6). Studies have shown that consumption of 8 to 15 mg of phenol could result in death (7). Phenol will quickly enter the circulatory system of the living due to its high permeability, regardless of the manner of exposure (skin contact or mucosal adsorption) (8). The presence of phenol in drinking water treated with chlorine leads to formation of side products and makes the water non-potable and harmful by giving it an unpleasant taste and odor (9). In addition, considering the carcinogenicity potential of phenol to humans and other living things, remarkable concerns are raised even in low concentrations (10). Toxic effects of phenol include penetration into the cells and cytoplasm, clotting and damaging the crucial cells in the body (10- 13). Thus, detection and determination of the concentration of phenolic compounds in wastewater and their subsequent removal in all steps of production, treatment and evacuation of wastewater into the sources appears to be necessary. Regulations of World Health Organization limits the phenol concentration to below $0.1 \mu\text{g L}^{-1}$ (ppb) and according to the regulations of MOEF (Ministry of Environment and Forests) its maximum allowed amount in the output of the industries and surface water is considered 1 mg L^{-1} (10, 14). When releasing wastewater into the surface water and for agricultural and drinking uses, the maximum allowed amount of phenol concentration is determined as 1 mg L^{-1} and $0.5 \mu\text{g L}^{-1}$ by Environmental Protection Agency Standard and Standard Institute of Iran, respectively (15, 16). Various processes are used for removal of phenolic compounds from aqueous media, most common of which include extraction, adsorption with activated carbon, steam distillation, electrochemical methods, radiation, advanced oxidation, chemical oxidation, adsorption, and biological treatment. The majority of these methods suffer from disadvantages such as high cost of treatment, the need for additional filtration, production of dangerous side products, low efficiency and applicability for a limited range of contaminant concentrations (17, 18). The adsorption process is one of the most common methods applied widely for removal of organic and inorganic contaminants from aqueous solution (19). The adsorption process is one of the simplest, most efficient, and cost effective alternatives for removal of phenol from aqueous media which is capable of removing most forms of organic material (19-23). The low costs and prevalence of the utilized adsorbents such as agriculture waste has led this method to be widely investigated and applied for phenol removal. Activated carbon, clay, polymer materials, sludge, zeolite, chitosan and chitin are some of the adsorbents used for phenol removal (24-31). Commercial activated carbon demonstrates high efficiency for removal of phenol, however, considering high costs of the preparation and reduction of commercial activated carbon, it is not cost effective to use. This has compelled researchers to try to develop novel cost effective adsorbents (32). Hence, in this study, the application of pomegranate peel ash is investigated as an adsorbent for removal of phenol from aqueous solutions.

2. Material and Methods

This study is carried out in Gonabad in 2016. All chemicals used in this study were purchased from Merck and Aldrich Companies. Dried peel of pomegranate was supplied from Ferdows city. To obtain carbon from these peels, they were first washed with clean water and then with deionized water. They were then dried in an oven at $105 \text{ }^\circ\text{C}$ for sixty minutes. In the next step, they were ground as finely as possible and placed in an oven at $450 \text{ }^\circ\text{C}$ for sixty minutes to obtain the carbon. The obtained carbon was ground in a porcelain mortar. It was then sieved using standard ASTM sieves with the size in the range of 0.15-0.85 mm. Finally, the samples were cooled and kept in a desiccator. To determine the optimum parameters for any kind of adsorbent, the experiments were performed on samples of water contaminated with phenol with concentrations of 10 to 100 mg L^{-1} , which were prepared from stock solution of 1000 mg L^{-1} of phenol, and initial pH values of 2 to 12 by addition of 0.1 and 1 normal sulfuric acid and sodium hydroxide. The monitoring took place by a Denver Ultra basic- UB10 pH meter made in USA. The adsorbent doses ranged within 0.1 to 0.7 mg L^{-1} at $23 \pm 2 \text{ }^\circ\text{C}$. Following addition of the adsorbent to the solutions in Erlenmeyer flasks, the mixture was stirred at constant temperature of $30 \pm 1 \text{ }^\circ\text{C}$ at stirring rate of 150 rpm using a stirrer equipped with incubator, model KS 4000i control, made by IKA Company of Germany. This process was repeated twice. Finally, the sampling of phenol concentration took place using a T80 UV/Vis spectrometer in 15 to 210 minutes after separation of the adsorbent by centrifuging at 4000 rpm for 10 minutes, and the calibration curve was plotted at wavelength 505 nm and evaluated on the basis of the equation $[\text{Phenol}] = 9.11 \times \text{ABS}_{505} - 0.756$, ($r = 0.99$) (8, 10). In the next step, the Langmuir and Freundlich adsorption isotherms were studied. The following equations were used to determine the adsorption capacity and efficiency (9): $q_e = (C_i - C_e)V / w$; Adsorption (%) = $(C_i - C_e) / C_i$
Where: q_e = adsorption capacity (mg/g), C_i = initial concentration of the adsorbed material in the solution (mg/L), C_e = equilibrium concentration of the adsorbed material after equilibrium takes place (mg/L), V = volume of liquid inside the reactor (L), W = Adsorbent mass (g).

3. Results

3.1. Investigation of pH effect on efficiency of the adsorbent

Figure 1 illustrates the impact of initial pH of the solution on phenol adsorption efficiency by pomegranate peel ash. As shown in Figure 1, the maximum phenol removal is obtained as 93.72% which occurs at pH=7.

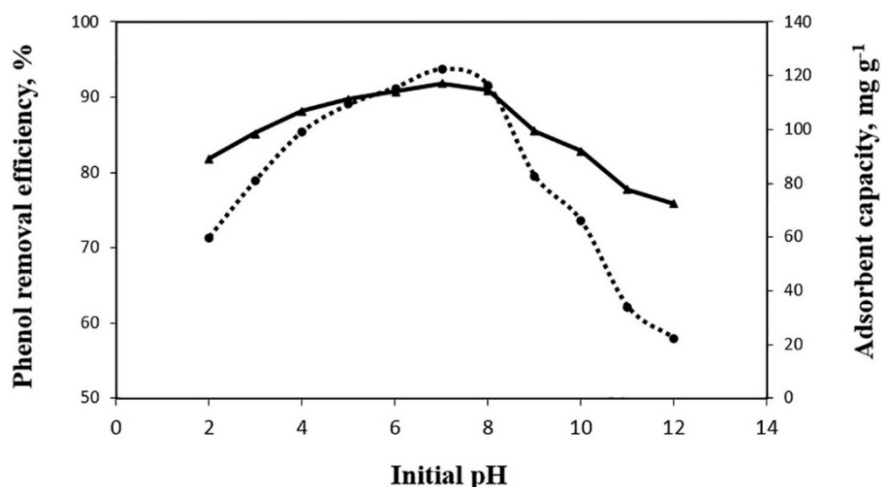


Figure 1. The effect of pH on phenol adsorption on pomegranate peel (initial phenol concentration 50 mg/l, adsorbent dosage 0.4 g/l, contact time 60 min)

3.2. Effect of the adsorbent dosage

As observed in Figure 2, the phenol removal efficiency increase from 69.7 to 97.06% with the increase of the adsorbent dose from 0.1 to 0.7 g/L. However, the adsorbed phenol rate decreases with respect to each gram of the adsorbent (adsorption capacity). Furthermore, once the adsorbent dose reaches above 0.6 g/L, a remarkable removal of phenol does not happen. Thus, the optimum dose of the adsorbent was chosen as 0.6 g/l and used in the next steps of the experiments.

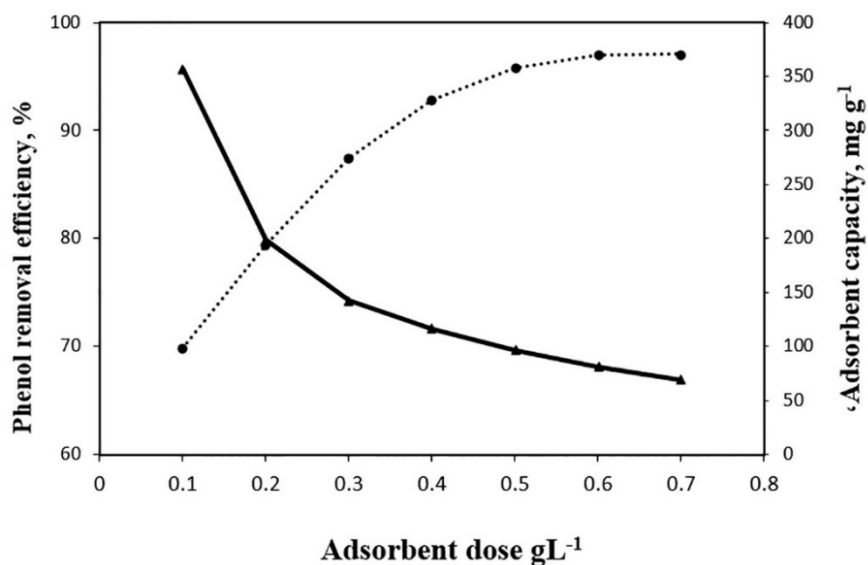


Figure 2. The effect of adsorbent dosage on phenol adsorption on pomegranate peel (initial phenol concentration 50 mg/l, pH 7, contact time 60 min)

3.3. Effect of contact time

The acquired results from the investigations demonstrate that, the adsorption capacity and phenol removal efficiency increases considerably at initial stages of the adsorption and after approximately 120 minutes reaches the maximum

amount (95.96%). The adsorption capacity of pomegranate peel ash was obtained as 79.97 mg/g. Therefore, the retention time of 120 minutes was chosen as the optimum time in this study (Figure 3).

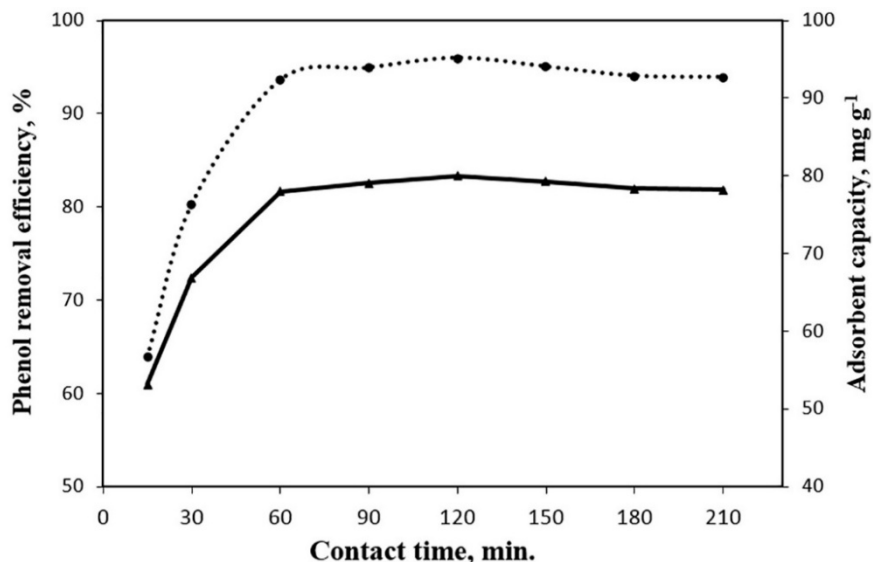


Figure 3. The effect of contact time on phenol adsorption on pomegranate peel (initial phenol concentration 50 mg/l, adsorbent dosage 0.4 g/l, contact time 60 min)

3.4. The effect of initial phenol concentration

As can be seen in Figure 4, the adsorption capacity of the adsorbent, increases with the increase of phenol concentration and reaches 148.38 mg/g at initial concentration of 100 mg from 16.43 mg/g at 10 mg. In contrast, the efficiency of phenol removal at the same time period demonstrates a reverse trend.

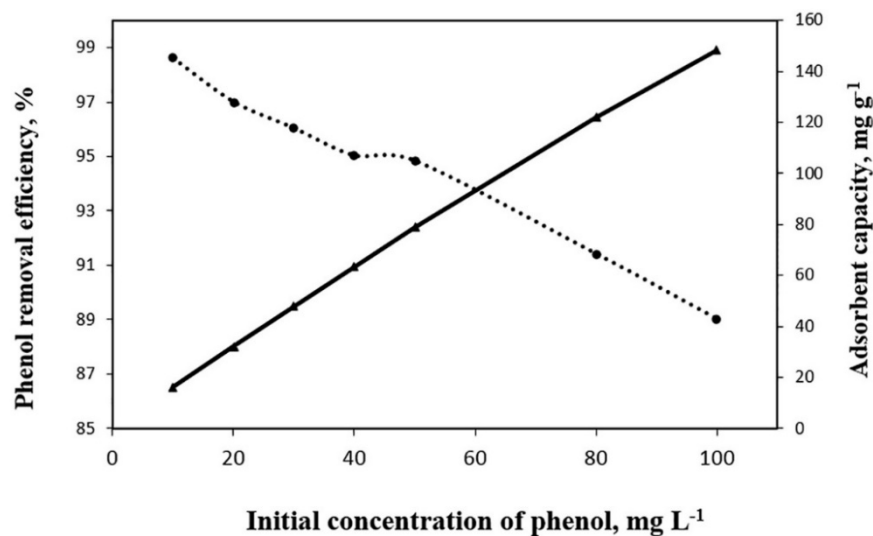


Figure 4. The effect of initial phenol concentration on phenol adsorption (initial phenol concentration 50 mg/l, adsorbent dosage 0.4 g/l, contact time 120 min)

3.5. Adsorption isotherm

The isotherm models turn experimental results into applicable formulas with useful parameters and make them easy to use in designing processes. Study of the isotherms may help interpret the reactions between the adsorbed material and the adsorbent. In other words, isotherm shows the relationship between concentration of the phenol in solution and the adsorbed phenol rate by solid phase when the two phases are in the equilibrium state. Langmuir and Freundlich equations are widely used in description of adsorption isotherms in solid/liquid systems. In Langmuir theory,

absorption happens in certain homogeneous places within the adsorbent. This model is used to estimate the maximum rate of uptake, the amount of which is obtained in the experiments. However, Freundlich isotherm is based on the adsorption on heterogeneous surfaces and unlike the Langmuir model, does not determine the maximum capacity of the adsorbent. Hence, it is applicable at medium to low concentrations. The isotherms are shown for both models in Figures 5 and 6 based on the experimental data and obtained parameters from non-linear regression.

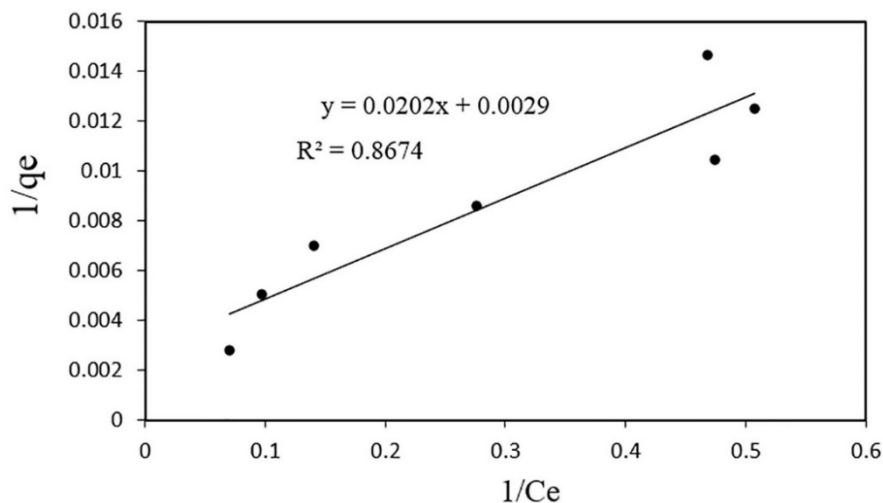


Figure 5. Langmuir isotherm of adsorption

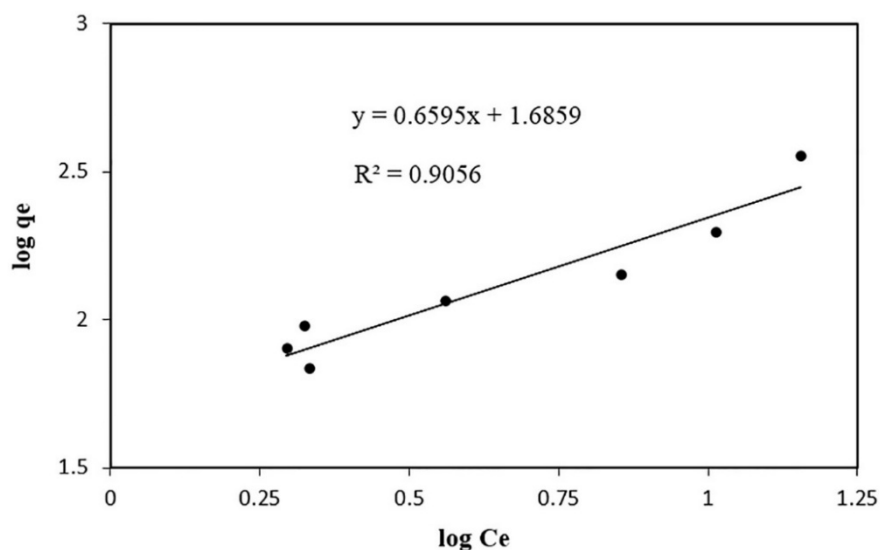


Figure 6. Freundlich of adsorption process

4. Discussion

4.1. The effect of pH

The pH of a solution plays an important role in adsorption process, especially in adsorption capacity. This results from the amount of surface charge of the adsorbent, amount of ionization of the material present in the solution as well as separation of the functional groups present in the adsorbing sites of the adsorbent (34). Thus, the adsorption of phenol was studied as a function of hydrogen ion concentration, to determine the effect of the initial pH variation of the samples on the phenol adsorption process by pomegranate peel ash. The initial pH values of the samples were adjusted within 2-12 in each series of the experiments. The utilized adsorbent was 0.04 g in 100 mL of the solution under experiment and the initial concentration of phenol was 50 mg L⁻¹ in all samples. As inferred from Figure 1, by increasing the pH value from 2 to 7, the phenol removal efficiency also increases to 93.72% from initial value of 71.4% and decreases the adsorption on polar adsorbents. Then, following increasing the pH value above 7, efficiency

of the process decreases, as in pH=12 the removal efficiency is obtained as 57.96%. In general, at higher pH values, adsorption decreases (pH>7) since phenol is in the form of a salt which loses its negative charge easily, and hence becomes difficult to adsorb. In addition, in this condition, the presence of OH⁻ ions inhibit phenol ions from being adsorbed (35).

4.2. The effect of adsorbent dosage

The adsorbent dose is one of the most important parameters which determine the adsorbent capacity for determination of phenol concentration. Therefore, the adsorption experiments were performed using an adsorbent dose in the range of 0.1-0.7 g in 100 mL solution containing 50 mg L⁻¹ at optimum pH=7 for sixty minutes at 23±2 °C, to determine the effect of adsorbent dose on the adsorption process by pomegranate peel ash. As observed in Figure 2, the efficiency of phenol removal has gradually increased up to 97.06% with a gentle slope, following increasing the adsorbent up to 0.7 g/L. In other words, there are still sites on the adsorbent which are not saturated during the adsorption process. Considering the fact that, the concentration of phenol is kept constant in all experiments, increasing the amount of the adsorbent has led to enhancing the ratio of the adsorbent to the adsorbed phenol, which provides more surface and sites for adsorption. Furthermore, the results show that, when adsorbent dose reaches above 0.6 mg/L, a remarkable enhance is not observed in phenol adsorption by the adsorbent. It seems, after increasing the adsorbent dose up to a certain amount, the maximum adsorption rate is reached and thus, from this amount on, the remaining amount of the contaminant will stay constant even after addition of more adsorbent (36). Although phenol removal increased by increasing the adsorbent dose, the adsorbed phenol rate per gram of adsorbent decreased, because concentration of dissolved phenol (50 mg/L) decreased by being adsorbed on unsaturated active sites of the adsorbent. On the other hand, the increase of the adsorbent results in agglomeration of the particles and their adherence to each other (37). Hence, the amount of 0.6 g/L of the adsorbent is chosen as the optimum dose of the adsorbent for the rest of the study.

4.3. The effect of contact time

The contact time is one of the most important parameters for determination of the equilibrium state of adsorption process. The impact of contact time on the adsorption process was studied at 23 ± 2 °C, with initial phenol concentration of 50 mg/L and an adsorbent dose of 0.6 g/L in time ranges between 15-210 minutes. Figure 3 depicts the impact of contact time on the adsorption capacity and efficiency of phenol removal by pomegranate peel ash. The adsorption capacity and efficiency of phenol removal increases at first stages of the adsorption remarkably, and then reaches the maximum amount (95.96%) after 120 minutes. The adsorption capacity of pomegranate peel ash is also obtained as 79.97 mg/g. Therefore, the retention time of 120 minutes is chosen as the equilibrium time. In general, removal of the adsorbed material is fast at first stages of the process, but then decreases gradually until reaching the equilibrium state. This phenomenon may be interpreted as; at the first stages of the adsorption process, there are many available sites on the surface of the adsorbent and over time, the unoccupied sites on the surface of the adsorbent are hardly occupied due to depletion forces between molecules of the adsorbent and the solution phase. On the other hand, the efficiency of phenol removal is high at first stages, because of the high availability of the sites on the surface of the adsorbent for adsorbing the contaminants. Once the sites on the surface of the adsorbent are saturated upon adsorption process, the adsorption rate is controlled by adsorption and desorption of the contaminants on the adsorbent (36). Similar results have been reported by Gengiz and Cavaz (37), and Senthilkumar et al. (38).

4.4. The effect of initial phenol concentration

Effect of initial concentration of phenol on the adsorption efficiency was studied at 23 ± 2 °C with the adsorption dose of 0.6 g/L for 120 minutes. As shown in Figure 4, the adsorption capacity of the adsorbent increases by increasing phenol concentration, whereas the efficiency of phenol removal demonstrates a reverse trend. When initial concentration of phenol increases to 100 mg/L from 10 mg/L, the adsorption capacity increases to 148.38 mg g⁻¹ from 16.43 mg g⁻¹. This may be explained as; with the increase of phenol concentration, the mass transfer driving force and hence the speed of phenol molecules passing through solution to the liquid layer surrounding the adsorbent and finally toward surface of the adsorbent, increases (40, 41). On the other hand, the efficiency of phenol removal (removal efficiency) decreases from 98.06% to 89.03 mg/L by increasing initial concentration of phenol from 10 mg/L to 100 mg/L. This could be attributed to the constant sites for adsorption and increasing the number of molecules of the adsorbed material. In addition, similar results are obtained for phenol adsorption from aqueous solutions by clay and other low price adsorbents (42-48).

4.5. The isotherms

Studying the isotherms may help interpret how reactions between the adsorbent and the adsorbed material take place. In other words, an isotherm demonstrates the relationship between phenol concentration of the solution and amount

of the phenol adsorbed by solid phase when the two phases are in equilibrium state. The Freundlich isotherm is an experimental relationship based on adsorption on heterogeneous surfaces and unlike the Langmuir model, does not specify the maximum adsorption capacity and thus, is applicable only at medium or low concentrations (49-51). The isotherms are shown in Figures 5 and 6 for both models on the basis of experimental data and parameters resulted from nonlinear regression. The correlation coefficient of the Langmuir model ($R^2=0.8674$) is lower than that of the Freundlich model ($R^2=0.9056$) which indicates the fact that the Freundlich model is more suitable for interpretation of equilibrium adsorption of phenol on pomegranate peel ash. On the other hand, once the parameter $1/n$ value is in between 0.1-1, it shows appropriate adherence to the Freundlich isotherm and indicates that the adsorption is pleasant as was in this study.

5. Conclusions

The acquired results demonstrated that pomegranate peel ash shows good capability for removal of phenol from aqueous solutions. The adsorption rate will increase by increasing the amount of the adsorbent due to contact surface increase. At higher concentrations of phenol, a decrease in adsorption rate was observed. The adsorption capacity obtained as 148.38 mg/g when applying 0.6 g pomegranate peel ash for removal of phenol from 100 mL of solution containing 100 mg of phenol in 120 minutes at pH=7. Furthermore, it was observed that, pomegranate peel ash is capable of removing more than 98% of the phenol from aqueous solutions with initial concentrations in between 10-100 mg/L. On the other hand, the obtained experimental results in this study were evaluated by two well-known models, Freundlich and Langmuir, and the coefficient values acquired indicate that the Freundlich model is more appropriate compared to the Langmuir model.

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Conflict of Interest:

There is no conflict of interest to be declared.

Authors' contributions:

All authors contributed to this project and article equally. All authors read and approved the final manuscript.

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