Continuous flow adsorption for phenol removal using environmentally friendly naturally derived bed

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Abstract
Phenol is one of the common contaminants observed in many wastewater industries. It is toxic, hazardous, carcinogenic and listed as a priority pollutant by the Environmental Protection Agency (EPA). This research aimed to establish the efficacy of activated carbon derived from walnut shell in extracting phenol from aqueous solutions using a fixed-green bed column adsorption system. The effect of parameters affecting the adsorption process including the initial concentration of phenol, bed ratio, and flow rate, was studied. The results showed that the highest percentage of phenol removal by the activated carbon is 86.2% at pH 7, initial concentration of phenol 0.001M, bed ratio 1:3 sand/activated carbon, and flow rate 10 ml/min. The breakthrough behavior of the fixed-bed adsorption process was studied. It was observed that the adsorption process equilibrium is practically reached after 105 minutes. The adsorption column dynamic behavior was investigated using three numerical models. The results confirmed that Thomas and Yoon-Nelson models are found more fitted to the adsorption experimental results. Moreover, modeling and interpretation of the column adsorption isotherms predicted that the Freundlich isotherm model is better than Langmuir isotherm model to describe the column adsorption data indicating that the phenol adsorbed molecules are not restricted to monolayer formation and the mechanism of adsorption is chemo-sorption. Briefly, the results of this study pointed out that the activated carbon derived from the walnut shell is not only a low-cost green adsorbent but also has high performance in the removal of phenol from aqueous solutions.

Keywords: Walnut Shell; Activated Carbon; Phenol Removal; Fixed-green bed column

1. Introduction
The growth of world's population, the huge increase in environmental pollution and the decrease in the sources of clean water have enforced the pollution prevention and environmental protection stakeholders to work intensively for reducing and regulating pollution.

Restricted instructions and rules are implemented by the Environmental Management Authority and the governments around the world, the rules are geared towards enforcing the leaders in industrial and municipal facilities to control and minimize the formation of waste products as well as hindering the disposal of sewage and wastewater in land and water sources without treatment [1].

Wastewater may contain large levels of pollutants including organic [2, 3, 4 and 5] and inorganic pollutants such as toxic chemicals [6,7] that may discharge from domestic and industrial facilities. These contaminants cause serious pollution of the aquatic environment and have negative impact on water quality making the water resources unusable suppliers for drinking water. Therefore, primary, secondary and tertiary treatments technique are applied, however, the final treatment methods may be some times not selective for specific contaminants besides they are not cost-effective. Accordingly, water treatment leaders have evolved considerably to imply new and cost-effective water treatment technologies. Among the technologies used is the adsorption technique, which becomes more popular purification process in recent years owing to its versatility selectivity and low cost. The term adsorption could be defined as the change in the concentration of a molecule in the surface layer of a solid material in comparison with the bulk phase with respect to unit surface area. The adsorption process involves the selective interaction of one or more compounds from the liquid phase on a solid called adsorbent. Separation by adsorption is highly effective, simple design, cheap, easy to adopt and scale-up compared to the other conventional treatment in water pollution control [8]. In addition to removing pollutants, the adsorbent can act as a particulate trap as well as a means of removing taste and odor.

Adsorption processes could be carried in different modes, nevertheless, adsorption is commonly held in column continuous processes which are more efficient than batch processes, it allows a more efficient use of the adsorbent, since the dynamic system enables an evaluation of the material saturation in relation to the time, space and length of the adsorption column [9].

New adsorbents have superior tendency to remove undesirable chemicals from hydrological systems are synthesized and employed, however the high cost and relative inability to regenerate
of some of them hinders their use at larger scales, hence, the main benefit of adsorption has been the use of low-cost materials, to reduce the cost of the procedure. Different types of adsorbents are usable including natural and synthetic clays like zeolites [10, 11]. Other types are the adsorbents could be derived from industrial and biogenic wastes like activated carbon and ashes [12, 13].

The utilizing of renewable, agricultural, and industrial materials and by-products as adsorbents is one of the tools for applying the green sustainability concepts in pollution remediation. Green adsorbents are eco-friendly materials, popular, and available in large quantities in most countries, they have been confirmed to act as cheap filters having high potential, strength, and selectivity to interact with contaminants such as dyes, heavy metals, phenols, pesticides and pharmaceuticals [14].

On another hand, Phenolic compounds exist in water bodies due to the discharge of polluted wastewater from industrial, agricultural and domestic activities. Phenol compounds are known to be toxic and inflict both severe and long-lasting effects on both humans and animals. They act as carcinogens and cause damage to the red blood cells and the liver, even at low concentrations. The interaction of these compounds with microorganisms, inorganic and other organic compounds in water can produce substituted compounds or other moieties, which may be as toxic as the original phenolic compounds [15].

Although numerous numbers of studies dealt with studying phenol adsorption by different adsorbents from aqueous mixtures, only a few studies focused on the fixed-green bed column adsorption processes. In the current work, activated carbon derived from walnut shell is used as adsorbents for phenol removal from aqueous solution using fixed bed down flow process.

2. Materials and Methods

2.1. Preparation and characterization of the green bed

Walnut shell was collected from household waste of Erbil Province gardens and mainly from Erbil city. After screening the shells and separation from impurities, in order to softening Walnut shells, walnut shells were placed for 24 hours in water rinsed and then dried for 5 hours at 105 °C in thermostatic oven. The dry shells were milled using electric mill and then were screened with
standard laboratory sieves. Particles with an average particle size of 0.38 mm were separated and immersed for two hours in acid solution (phosphoric acid $H_3PO_4$) for the purpose of chemical activation. The activated shells were then carbonized in an ash furnace at 500°C for 60 min in the presence of carbon dioxide gas. In the final stage, the activated material was washed various times with distilled water at 100°C to remove the excess reagent used in the chemical activation until the pH of the water had reached around 7.0. Finally, the activated carbon was dried (in an oven at 110°C) for 24 hours, cooled and then used as the green adsorbent bed. Figure 1 shows the steps of preparation the green bed. The prepared bed was characterized; the characteristic of the adsorbent is illustrated in Table 1.

![Figure 1. Preparation steps of the activated carbon](image)

Table 1. Characteristics of the activated carbon from walnut shell

| Parameter                  | Value | Specific surface area (m²/g) | Average pore diameter (nm) | Porosity % | pH  | Iodine no. (mg/g) | Ash content % |
|----------------------------|-------|------------------------------|----------------------------|------------|-----|------------------|---------------|
| Bulk density (kg/m³)       | 792   | 765                          | 46.6                       | 32.9       | 3.3 | 622              | 4.4           |

The adsorbent shows high specific surface area and pore volume which indicated that it has promising adsorption efficiency.

2.2. Preparation of the adsorbate (phenol solution) & absorbance determination

A stock solution of phenol 0.001M was prepared by dissolving predetermined amounts of phenol in distilled water. This solution was diluted as required to obtain standard solutions. The
absorbance of the solutions was determined by UV-Visible spectrophotometer between 200 and 750nm. The standard calibration curve is then plotted.

2.3 Fixed green bed column adsorption Study

Figure 2 show a schematic diagram for the adsorption process and of the experimental set up used for column studies. For column operation, a laboratory scale column of diameter 5.5 cm and height of 100 cm was used. A mixture of the prepared activated carbon and a sample of pure sand was prepared; the sand was used as a carrier filler to increase the porosity of the bed. The mixture was filled in the column containing thin layer of gravel aggregate of 1.5 mm diameter packed at the bottom for support. The bed was filled up to a specific height in the column. Another thin layer of gravel was charged to be settled at the top of the bed. The average adsorbent particle size was 0.38 mm and that of sand was 4.75 mm.

First, 500 mL of distilled water was passed through the packed bed to obtain more compact packing. For all the experiments, aqueous phenol solution (0.001M) was prepared and allowed to down flow by gravity through the bed. The treated effluent was collected at the bottom at 30 minute time interval and analyzed. The initial phenol solution and the collected effluent samples were submitted to UV-Visible spectrophotometer analysis with the objective of verifying the quantity of phenol that had been adsorbed. The absorbance of the solutions was determined between 200 and 750nm.

![Figure 2. The experimental continuous adsorption set-up](image)
The percent of removal efficiency (R%) was calculated using equation (1)

\[
R\% = \left(\frac{C_o - C_e}{C_o}\right) \times 100
\]  

(1)

Where \( C_o \) is the initial conc. of phenol solution, \( C_e \) is the conc. of the effluent after treatment.

The parameters varied in the continuous experiments were (bed ratio = green adsorbent/sand): 1:2, 1:3, 1:4, 1:5, 1:6 and phenol solution flow rate (10-60mL/min) and initial concentration of aqueous phenol solution (2-12)µg/ml. The effluent pH was kept constant (pH=7). The results were organized to make graphics, in order to better observe the adsorption behavior.

3. Numerical modeling for studying the column adsorption dynamics

In this study, the rate of adsorption was studied by employing three models. The models are Bohart-Adams, Thomas, and Yoon-Nelson. The models are used to predict the dynamic behavior of the fixed-bed column [16, 17].

Bohart – Adams model is based on the surface reaction theory and describes the initial part of the breakthrough curve. The model equation is displayed in equation 2:

\[
\ln\left(\frac{C_t}{C_o}\right) = k_{AB}t - k_{AB}N_0 \frac{Z}{U_0}
\]  

(2)

where \( C_0 \) and \( C_t \) (mg/L) are the inlet and effluent concentrations, \( k_{AB} \) (L/mg.min) is the mass transfer coefficient, \( t \) (min) is the service time, \( N_0 \) (mg/L) is the saturation concentration, \( U_0 \) (cm/min) is the linear velocity calculated by dividing the flow rate by the column cross-sectional area, and \( Z \) (cm) is the bed depth. The model parameters are obtained from the intercept and slope of a linear plot of \( \ln(C_t/C_0) \) against \( t \).

The Thomas model is based on the assumption that the process follows Langmuir kinetics with no axial dispersion in the column adsorption. The linearized form of the Thomas model is shown in equation 3:
\[
\ln \left( \frac{c_0}{c_t} - 1 \right) = \frac{k_{Th} q_o w}{Q} - k_{Th} C_o t
\]

(3)

Where \( k_{Th} \) is the Thomas model constant (ml min\(^{-1}\) mg\(^{-1}\)), \( q_o \) is the equilibrium adsorption amount of adsorbate (mg\(^{-1}\)), \( w \) is the mass of the adsorbent (g), and \( Q \) is the flow rate (ml min\(^{-1}\)).

The theory of Yoon and Nelson model supposed that the rate of probability decrease in adsorption for each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The model equation for a single component system can be written as in equation 4:

\[
\ln \left( \frac{c_t}{c_o - c_t} \right) = k_{YN} t - \tau k_{YN}
\]

(4)

where \( k_{YN} \) (min\(^{-1}\)) is the rate velocity constant, and \( \tau \) (min) is the time required for 50% adsorbate breakthrough (i.e. \( C_t/C_0 \approx 0.5 \)). From the linear dependence of \( \ln[C_t/(C_o - C_t)] \) versus \( t \), the model parameters can be determined.

4. Modeling of the adsorption isotherms

Two isotherm models have been used for the equilibrium modeling of the adsorption system. The Langmuir isotherm model which is predicated on the assumption that there are limited numbers of active sites homogeneously spread through the adsorbent surface. This active site has the same tendency for single-layer adsorption molecules, so there is no contact with the adsorbed molecules. The Freundlich isotherm model refers to adsorption on heterogeneous surfaces by an association with the adsorbed molecules, not restricted to single layer formation (multilayer adsorption processes) [18, 19]. The linear form of the Langmuir and Freundlich equations can be written as in equations 5 and 6 respectively:

\[
\frac{c_e}{q_e} = \frac{1}{Q_o k} + \frac{c_e}{Q_0}
\]

(5)
\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \] (6)

Where \( q_e \) is the amount of adsorbate at equilibrium per gram of adsorbent (mg/g), \( C_e \) the equilibrium concentration of sorbate in the solution (mg/L), \( Q_0 \) and \( K \) are Langmuir constants related to sorption capacity and sorption energy, respectively. \( K_f \) and \( 1/n \) are the Freundlich model constants.

5. Results and discussion

Adsorption processes for decontamination of wastewaters can be carried out either discontinuously in batch reactors or continuously in fixed-bed reactors or columns. Fixed-bed systems have an important advantage because adsorption depends on the concentration of the solute in the solution being treated [20]. The adsorbent is continuously in contact with fresh solution; hence the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant. Other advantages are higher residence times and better heat and mass transfer characteristics compared to batch processes [21].

The effect of some parameters, namely, volumetric flow rate, ratio of the green packing material (adsorbent/sand) and initial concentration of the adsorbate was studied. Volumetric flow rates relate to the effective contact time between sorbate and sorbent in the column, thus influencing the mass transfer rate. Six distinct volumetric flow rates (10, 20, 30, 40, 50 and 60 mL/min) for a preset green bed/sand ratios (1:2, 1:3, 1:4, 1:5, 1:6) and constant feed composition in aqueous stream were studied. The initial concentration of phenol in the feed stream governs the rate of mass transport, while the green bed/sand ratios is a crucial determinant which governs the capacity and life of an adsorption column which are required for successful application.

Figure 3 illustrates the variation of phenol removal efficiency % with flow rate of phenol solution with a constant influent concentration 0.001M in presence of 1:1 green bed/sand ratio. It is obvious to note that as flow rate increases percent removal efficiency decreases. It is understandable to figure out that at lower flow rates, phenol species have enough time to diffuse through the pores of the adsorbent material and hence occupy more sites and hence results in maximum utilization of adsorption bed region. The situation is similar to the findings in other
research work found in literature [22, 23, 34, and 25]. An increase in flow rate decreases the contact time of the adsorbent and the phenol molecules causing reduction in adsorption capacity and service time of the bed.

Figure 3. Variation of Removal efficiency % with the volumetric flow rate of the influent

Figure 4 shows the relation between ratios of the green adsorbent/sand with a constant influent concentration 0.001M = 94 mg/L, contact time 30 min. and flow rate of 20 mL/min. It is clear that the optimum removal efficiency obtained with using of mixture of (3 parts of the green bed and one part of sand). The increase in percentage adsorption may be related to the fact that the number of available active adsorption sites increases by increasing the adsorbent [17] resulting from a widened mass transfer zone formation. The decrease of removal efficiency % when using more than 3 parts of the adsorbent may be attributed to the restricted availability the active adsorption sites on the green bed. The results confirm that the sand which acts as a carrier has a role in prevention the agglomeration of the particles of the green adsorbent.
Figure 4. Effect of bed ratio on removal efficiency %.

The results obtained concerning the breakthrough behaviors of fixed-green bed column adsorption process on % removal of phenol are represented Figure 5. It is obvious to note that, breakthrough curves exhibit a characteristic ‘S’ shape but with a specific degree of steepness. The equilibrium is practically reached at 105 minutes. The results obtained show that the plot has two steps; the first is rapid and the second is a slow one. This relates to the great availability of the free active sites of the adsorbent at the beginning of the experiment and which becomes less available as time proceeds.

Figure 5. Removal efficiency % of phenol versus time.
The results regarding the numerical modeling for column adsorption dynamics are illustrated in Figures 6, 7 and 8. The plot of Bohart-Adams model is shown in Figure 6. The Yoon-Nelson model plot is illustrated in Figure 7, while Thomas model plot is displayed in Figure 8.

![Figure 6. The plot of the Bohart-Adams model.](image1)

![Figure 7. The plot of Yoon-Nelson model.](image2)

![Figure 8. The plot of Thomas's model.](image3)

The plots of the numerical models predicted that the three models could be used to explain the dynamic behavior of the column adsorption of phenol on the activated carbon bed derived from walnut shell waste. This was reflected by the high regression factors of the plots. However, Thomas and Yoon-Nelson's models are more fitted to the experimental results ($R^2$ for both = 0.9163) which indicates that they are more capable to forecast the dynamic behavior in the adsorption column.

The equilibrium modeling of the adsorption system in the current work is figured out using
Langmuir and Freundlich adsorption isotherms plotted in Figures 9 and 10 respectively.

The two equilibrium adsorption models parameters estimated from the plots are listed in Table 2.

Table 2. Langmuir and Freundlich isotherm model parameters

| Adsorption Isotherm Model Type | Parameters                                      | Parameters                                      | $R^2$          |
|-------------------------------|-------------------------------------------------|-------------------------------------------------|----------------|
| Langmuir                     | Maximum adsorption capacity $q_m = 8.01$ (mg/g) | Energy of adsorption $b = -0.2643$ (ml/mg)     | $R^2 = 0.8734$ |
| Freundlich                   | $n = $ adsorption intensity                      | Adsorption capacity $K_f$, $\ln K_f = 6.66$    | $R^2 = 0.9119$ |
|                              | $1/n = 1.8285$                                  | $K_f = 785.87$                                 |                |
|                              | $n = 0.546$                                     |                                                 |                |

The Langmuir parameters include ($q_m$, $b$, and $R^2$), while Freundlich parameters include ($K_f$, $1/n$ and $R^2$). It is worthy to note that the value of $R^2$ (0.9119) of Freundlich isotherm is slightly higher than the value of $R^2$ (0.8734) of Langmuir isotherm, this indicates that Freundlich isotherm model is more capable to fit the experimental data compared to Langmuir isotherm model. Matching the experimental results with Freundlich isotherm indicated a multilayer adsorption of phenol on the surface of walnut shell activated carbon. The value of $n$ indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n= 1$, then adsorption is linear; if $n$ is $< 1$ as it is in the current work, then adsorption is a chemical process.
[19] The numerical value of $1/n > 1$ indicates that adsorption capacity is only slightly suppressed at higher equilibrium concentrations.

6. Conclusions

The fixed green bed down flow adsorption process for phenol removal from aqueous solutions is feasible and effective by using a walnut shell activated carbon as green adsorbent derived from natural waste. The bed is cost-effective and environment friendly as it derived from biomass; a natural waste that is considered as a source of pollution. The natural waste has been reused in the current work to produce the green adsorbent instead of disposing it in landfills. The adsorption process could be scaled up to industrial level simply and used for removal of phenol compounds from wastewater. The initial concentration of phenol solution, its volumetric flow rate and the mass of the green bed seemed playing vital role on the adsorption capacity of the bed. The dynamic of the column adsorption and the adsorption isotherms could be studied using numerical models developed for such purposes. The adsorption of phenol on the green bed using the down flaw mode seemed to be multilayer kept on via chemo-sorption mechanism. A comprehensive study on the green bed regeneration as well as the adsorption kinetics will be the items of a future study.
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