Adsorption of 4-chlorophenol from aqueous solution using activated carbon synthesized from aloe vera green wastes

Yusef Omidi-Khaniabadi¹, Ali Jafari¹, Heshmatollah Nourmoradi², Fatemeh Taheri¹, Seddigheh Saeedi¹

¹ Department of Environmental Health Engineering, School of Health, Lorestan University of Medical Sciences, Khorramabad, Iran
² Department of Environmental Health Engineering, School of Health, Ilam University of Medical Sciences, Ilam, Iran

Abstract
In this study, activated carbon synthesized from Aloe vera green wastes was used as a sorbent to remove 4-chlorophenol (4-CP) from aqueous solutions. The influence of contact time (0-100 minutes), pH (2-8), adsorbent dosage (1-9 g/l), and initial 4-CP concentration (10-60 mg/l) in batch system was investigated on the sorption. The sorbent was specified using scanning electron microscopy (SEM). Equilibrium for 4-CP sorption was reached at contact time of 40 minutes. The pH of 2 was also found to be the optimum pH in the sorption process. Fitting the experimental data to different kinetic and isotherm models illustrated that the experimental data was well fitted by pseudo-second order kinetic ($R^2 > 0.98$) and Freundlich isotherm ($R^2 > 0.99$) models. According to the results, activated carbon prepared from Aloe vera green wastes is a low-cost effective option for the sorption of 4-CP from aqueous solutions.

KEYWORDS: Adsorption, Aloe Vera, 4-chlorophenol, Kinetics

Date of submission: 19 Oct 2014, Date of acceptance: 24 Jan 2015

Introduction
Water pollution due to industrial activities has been considered as one of the most important problems in the current century, especially in developing countries.¹ Phenol and phenolic compounds have been listed as priority pollutants in water and wastewater because of their high toxicity and low biodegradability.²⁻⁴ The principal sources of environmental pollution with chlorophenols are effluent from petrochemical units, coal gasification sites, oil refineries, and pharmaceutical industries.⁵ A phenolic compound recognized as a priority pollutant by the United States Environmental Protection Agency (USEPA) due to its toxicity, carcinogenicity, and mutagenicity to living organisms is 4-chlorophenol (4-CP).⁵⁻⁷ The maximum permissible limit of 4-CP in potable water is 0.5 mg/l.⁵ Normally, 4-CP is not degraded through biological treatment in aqueous media. Therefore, many techniques such as electrochemical oxidation, photocatalytic degradation, ultra-filtration, wet oxidation, solvent extraction, and membrane separation and adsorption have been used to remove 4-CP from aqueous solutions.⁸⁻¹⁰ Among the physicochemical methods, adsorption process has been widely applied as a treatment technique for organic pollutants.¹¹,¹² This method is one of the best treatment alternatives...
for the removal of pollutants like 4-CP from water and wastewater, because it is possible to recover the sorbent and adsorbate. Adsorption onto activated carbon due to its simple application and high sorption capacity is the most commonly used technique for the removal of toxic organic pollutants. However, sorption by commercial activated carbon is expensive. Therefore, researches on the production of activated carbon from cheap, local, agricultural wastes, especially due to its low-cost have gained attention worldwide. In addition to activated carbon, use of some adsorbents such as carbon black, XAD-4 resin, surfactant-modified natural zeolite, immobilized soybean peroxidase, chitosan, pumice treated with cationic surfactant, Amberlite XAD-16 resin, perlite, bentonite, and Azolla filiculoides biomass has been reported for 4-CP removal from aqueous solutions. The Aloe vera plant is grown in warm tropical areas such as India, United States, Mexico, Australia, Africa, South America, and Iran. Aloe vera green waste is the by-product of the agricultural industry and its original material is used in the production of latex and drugs. In this study, Aloe vera green waste was used as a low-cost sorbent in the production of activated carbon for the removal of 4-CP from synthetic wastewater. The influence of parameters such as contact time, pH, adsorbent dosage, and initial concentration was investigated on the sorption.

### Materials and Methods

All Aloe vera green waste used in this study was collected from suburban farms of Ahvaz, Iran. 4-CP, H$_2$SO$_4$, and NaOH were purchased from Merck Co. (Germany). Through the addition of 0.1 N H$_2$SO$_4$ or NaOH, the solution pH was adjusted using a pH meter (50-pp-sartorius model). All of the other chemical substances used were of analytical grade. The stock solution of 4-CP (1000 mg/l) was prepared by dissolving 1 g of 4-CP in 1 l deionized water and the working solutions were prepared by dilution of the stock solution. 4-CP has a chemical formula of C$_6$H$_5$ClO and molecular weight of 128.56 g/mol. The suspension of sorbent and adsorbate was agitated using a rotary shaker (Behdad-Rotomix Model) at 200 rpm.

Elemental analysis of samples of Aloe vera green waste-based activated carbon was conducted using a Heraeus Elemental Analyzer (Jobin-Yvon Ultima ICP-AES, USA). The surface morphology of the sorbent before and after adsorption process was characterized by a scanning electron microscope (SEM, Jeol Jsm-T330, Japan). The concentration of 4-CP in the solution was measured by an UV-Vis spectrophotometer (PG Instrument Limited Model) at maximum absorbance wavelength of 280 nm.

Aloe vera green wastes were thoroughly washed with deionized water for the removal of impurities and dried in an oven at 150 °C for 24 hours. Then, it was crushed using a Thomas-Wiley Laboratory Mill and sieved. The activated carbon with particle sizes of 300-600 µm was carbonized in a furnace at 550 °C for 20 minutes and sieved (mesh no = 40) for later experiments.

Batch sorption experiments were conducted to determine the influence of parameters such as contact time (0-100 minutes), pH (2-8), adsorbent dosage (1-9 g/l), and adsorbate concentration (10-60 mg/l) on the sorption of 4-CP from aqueous solutions using activated carbon from Aloe vera green wastes. All of the adsorption experiments were carried out at room temperature (25 °C) and shaken (200 rpm) with 100 ml 4-CP solution in a 250 ml Erlenmeyer flask. After agitation, the suspension was filtered using fiberglass paper and the sample absorbance was measured to determine 4-CP content. The experiments were duplicated and the average values were considered. The adsorption capacity of 4-CP was calculated using equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m}$$  (1)
Where \( q_e \) (mg/g) is the sorption capacity of Aloe vera green waste-based activated carbon, \( C_0 \) and \( C_e \) (mg/l) are the initial and equilibrium adsorbate concentrations, \( V \) (l) is the volume of the solution and \( m \) (g) is the mass of adsorbent.

### Results and Discussion

#### Characterization

Chemical composition of activated carbon derived from Aloe vera green waste showed that O, Ca, K, and Mg formed 92.7% of the total weight (wt%) of the sorbent. Other minor compounds included Na (5.92%) and Cl (1.35%).

Figures 1 (a) and (b) illustrate the surface morphology of the sorbent before and after the sorption. As seen in figure 1 (a), before the sorption, the surface morphology of activated carbon has uneven cavities and fine open pores. A regular structure and developed pores can be seen after the sorption in figure 1 (b), which shows a smoother surface of activated carbon. The development of pores can be due to the effect of 4-CP that has filled the pores.

#### Effect of contact time

The sorption data versus contact time for the uptake of 4-CP by Aloe vera green waste-based activated carbon is indicated in figure 2 (a). It can be seen that at first initial adsorption of 4-CP occurred rapidly. Equilibrium was obtained at contact time of 40 minutes (\( q_e = 5.59 \) mg/g), and then, gradually reached a fixed state during the remaining time of up to 100 minutes. The fast uptake of 4-CP molecules at the beginning of the adsorption time can be due to the availability of large numbers of vacant sites on the sorbent surface. With the increasing of contact time these vacant sites were saturated with 4-CP and adsorption capacity was gradually increased. Similar results were obtained for the removal of 4-CP by various adsorbents.\(^{5,16,18}\)

Zazouli et al. reported that the optimum contact time for removal of 4-CP from aqueous solution by Azolla filiculoides biomass was obtained at 75 minutes.\(^{22}\) Bilgili showed that the sorption of 4-CP from aqueous media by XAD-4 resin reached equilibrium at contact time of 120 minutes.\(^{15}\) Therefore, in this study, the contact time of 40 minutes was selected for the subsequent experiments.
Kinetic study

Kinetic models are suitable for designating the sorption mechanism of 4-CP on the adsorbent surface. In this study, the experimental data was fitted by pseudo-first order and pseudo-second order kinetic models in order to attain a better understanding from the sorption process and the results are presented in table 1. The pseudo-first order kinetic model $^{24-26}$ can be illustrated by equation (2):

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (2)

Where $q_e$ and $q_t$ (mg/g) are the values of 4-CP adsorbed onto the activated carbon surface at equilibrium and at time $t$ (minute), respectively. Moreover, $K_1$ (1/minute) is the rate constant of the pseudo-first order kinetic model. $K_1$ and $q_e$ were determined from linear plot of $\ln(q_e - q_t)$ versus time (minute), which are obtained from the slope and intercept, respectively.

The experimental data of 4-CP sorption was also analyzed using pseudo-second order kinetic model.$^{24,27}$ This sorption kinetic model can be shown by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (3)

Where $q_e$ and $q_t$ (mg/g) are similar to the pseudo-first order kinetic model, and $K_2$ (g/mg. minute) is the rate constant of the pseudo-second order kinetic. $K_2$ and $q_e$ can be obtained from the intercept and slope of $\frac{t}{q_t}$ against time in equation 3, respectively.

Figures 2 (b) and (c) show the pseudo-first order and pseudo-second order kinetic models for the adsorption of 4-CP from aqueous solutions by activated carbon obtained from Aloe vera green waste. The higher liner correlation coefficient ($R^2 > 0.98$) of the pseudo-second order kinetic model showed that the pseudo-second order kinetic model fitted the experimental data better than other kinetic models described earlier. Ahmed and Theydan showed that the removal of 4-CP from aqueous solution using activated carbon from Albizia lebbeck seed pods followed the pseudo-second order kinetic model.$^5$ Zazouli et al. also illustrated that the equilibrium data of 4-CP removal using Azolla filiculoides biomass was well described by the pseudo-second order kinetic model.$^{22}$ These results are in agreement with those reported by Tseng and Tseng$^{28}$ and Wu et al.$^{29}$ for 4-CP adsorption on activated carbons prepared from different agricultural precursors.

Effect of solution pH and adsorbent dosage

The solution pH is a substantial parameter in the sorption system.$^{30}$ The solution pH has a control effect on the ionization, dissociation, nature, and surface properties of the sorbent.$^{31}$

![Figure 2. (a) Effect of contact time on the sorption of 4-CP (adsorbent dosage = 3 g/l, and initial concentration = 20 mg/l at the initial solution pH), and (b) pseudo-first order and (c) pseudo-second order kinetic models](http://jaehr.muk.ac.ir)
Table 1. Parameters of pseudo-first order kinetic and pseudo-second order kinetic models

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$, experimental (mg/g)</td>
<td>$K_1$ (1/minute)</td>
</tr>
<tr>
<td>4-CP</td>
<td>5.85</td>
<td>0.0069</td>
</tr>
</tbody>
</table>

Figure 3. (a) Effect of pH on the adsorption of 4-CP (contact time = 40 minutes, adsorption dosage = 3 g/l, and initial concentration = 20 mg/l) and (b) effect of adsorbent dosage on the adsorption of 4-CP (contact time = 40 minutes, initial concentration = 20 mg/l, and pH = 2)

The influence of pH on the removal of 4-CP was investigated and the results are illustrated in figure 3 (a). As can be seen, the increasing of solution pH had a significant effect on the decreasing of 4-CP sorption by activated carbon. This result may be due to change in surface charge of 4-CP molecules and functional groups of the sorbent. The isoelectric point of the natural sorbent was found to be at pH of 11.3. At the lower pH values of the isoelectric point, there is a positive charge on the sorbent surface which will promote reaction with 4-CP. Radhika and Palanivelu reported that at a pH of 2, the adsorbent surface has more positively charged sites, but with the increase in solution pH, the sorption of 4-CP decreases. Thus, the optimum pH for the removal of 4-CP by carbon in this study was chosen as a pH of 2.

The effect of different dosages of Aloe vera green waste-based activated carbon was evaluated in an initial 4-CP concentration of 20 mg/l at room temperature and the results are presented in figure 3(b). It was observed that with increasing the adsorbent dosage from 1 g/l to 9 g/l, the adsorption capacity was reduced. The decrease in the sorption value of 4-CP in higher dosages of Aloe vera green waste activated carbon may be due to the unavailability of the pollutant molecules and their inability to cover all the active sites on the adsorbent surface. In other words, a large number of the surface active sites of the adsorbent cannot reach saturation state at high Aloe vera green waste activated carbon dosages. Therefore, a 1 g/l dose of Aloe vera green waste activated carbon was chosen as the optimum dosage for the next stages. Bilgili illustrated that the sorption of 4-CP from aqueous media remained almost constant at sorbent dosages greater than 10 g/l.

Effect of initial concentrations of 4-CP
The influence of initial concentrations of 4-CP on the sorption capacity was investigated and the results are illustrated in figure 4 (a). It is
evident that the sorption capacity of activated carbon prepared from Aloe vera green waste rapidly increased with the increasing of 4-CP in the solution. This can be due to accessibility of vacant sites of the adsorbent surface and increase in the driving force of 4-CP including the van der Waals force to the active sites of the adsorbent; this state can occur at higher 4-CP concentrations.

Isotherm study
When the sorption process reaches an equilibrium state, the study of adsorption isotherms is necessary in order to explain the distribution of adsorbate molecules between liquid and solid phases. Moreover, the isotherms can provide information about the heterogeneity and homogeneity of the adsorbent surface. In this study, the experimental data were analyzed by Langmuir, Freundlich, and Tempkin isotherms in initial concentration of 10-100 mg/l at contact time of 12 hours and the results are presented in table 2.

The Langmuir isotherm assumes that monolayer uptake occurs at binding sites with homogenous energy levels. This isotherm model predicts the maximum sorption capacity of 4-CP on the homogenous surface of Aloe vera green waste-based activated carbon. The Langmuir isotherm can be linearized using equation (4):

\[ \frac{C_e}{q_e} = \left( \frac{1}{bQ_m} \right) + \frac{C_e}{Q_m} \]  

(4)

Where \( C_e \) (mg/l) is the equilibrium concentration of 4-CP, \( q_e \) (mg/g) the sorption capacity of Aloe vera green waste activated carbon in during the equilibrium time. \( Q_m \) (maximum adsorption capacity, mg/g) and \( b \) (the Langmuir constant, l/mg) are obtained from the slope and intercept of linear plots of \( C_e/q_e \) versus \( C_e \), respectively.

The essential property of the Langmuir isotherm model is a dimensionless constant separation factor, \( R_L \), or equilibrium parameter and is defined by equation (5):

\[ R_L = \frac{1}{1 + bC_0} \]  

(5)

Where \( b \) is the Langmuir constant and \( C_0 \) is initial adsorbate concentration (Langmuir isotherm). The value of \( R_L \) demonstrates that the sorption system is unfavorable (\( R_L > 1 \)), irreversible (\( R_L = 0 \)), liner (\( R_L = 1 \)), or favorable (\( 0 < R_L < 1 \)). Based on the value of \( R_L \) (0.92), the sorption system of 4-CP on the activated carbon was favorable.

The Freundlich isotherm model can be applied for non-ideal adsorption on heterogeneous surface of sorbent. The Freundlich isotherm model can be described by equation (6):

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

(6)

Where \( q_e \) is the sorption capacity, \( C_0 \) is initial adsorbate concentration (Langmuir isotherm), \( K_f \) (l/g) and \( n \) are constants of the isotherm and illustrate the capacity and intensity of the adsorption, respectively. In this isotherm model, \( n \) demonstrates the adsorption intensity. \( K_f \) and \( n \) are obtained from the intercept and slope of plotting \( \ln q_e \) versus \( \ln C_e \), respectively. The values of \( n \) higher than 1 illustrate that the sorption bonds between pollutant and adsorbent surface have been powerfully formed. An \( n \) value higher than 1 and less than 10 shows that the adsorption process is suitable. In this study, the value of \( n \) calculated using the Freundlich model was 1.13. Therefore, the value of \( n \) illustrated that the adsorption bonds between 4-CP and Aloe vera green waste activated carbon was appropriately strong. Figures 4 (b) and (c) show the Langmuir and Freundlich isotherm models plot for the adsorption of 4-CP on the activated carbon surface.

Tempkin illustrates the influence of some indirect sorbate/adsorbate interactions on the adsorption isotherm. The Tempkin isotherm is applied through equation (7):
\[ q_t = B_1 \ln K_t + B_2 \ln C_e \] (7)

Where \( q_e \) (mg/g) is the adsorption capacity at equilibrium time, \( C_e \) (mg/l) is the equilibrium concentration of 4-CP, and \( B_1 \) and \( K_t \) are Tempkin constants. Amounts of \( B_1 \) and \( K_t \) are calculated from the plot of \( q_e \) versus \( \ln C_e \). Figure 4 (d) shows the Tempkin isotherm model plot for the sorption of 4-CP. The adsorption isotherm model of 4-CP by Aloe vera green waste activated carbon was well described by the Freundlich isotherm. Similar results were reported by Radhika and Palanivelu for the removal of 4-CP from aqueous solution using coconut shell activated carbon.\(^{32}\) Kuleyin reported that the experimental data of 4-CP removal using surfactant-modified natural zeolite are well described by the Freundlich isotherm model.\(^{16}\)

![Figure 4](http://jaehr.muk.ac.ir)

**Figure 4.** (a) Effect of initial concentration on the adsorption of 4-CP (contact time = 40 minutes, adsorption dosage = 1 g/l, and pH = 2) and (b) Langmuir, (c) Freundlich, and (d) Tempkin isotherms

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>( b ) (l/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>4-CP</td>
<td>47.6</td>
<td>0.0042</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 2. Parameters of Langmuir, Freundlich, and Tempkin isotherms
Table 3. Comparison of the maximum monolayer adsorption capacities of 4-CP with activated carbon from various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum sorption capacity (mg/g)</th>
<th>Contact time (h)</th>
<th>Temperature (°K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aloe vera green waste-based activated carbon</td>
<td>47.60</td>
<td>12.00</td>
<td>298</td>
<td>This study</td>
</tr>
<tr>
<td>Zeolit</td>
<td>12.70</td>
<td>8.00</td>
<td>293</td>
<td>16</td>
</tr>
<tr>
<td>Azolla filiculoides biomass</td>
<td>8.24</td>
<td>1.15</td>
<td>298</td>
<td>22</td>
</tr>
<tr>
<td>Rice husk</td>
<td>44.64</td>
<td>2.00</td>
<td>288</td>
<td>38</td>
</tr>
<tr>
<td>Cork</td>
<td>93.84</td>
<td>168.00</td>
<td>298</td>
<td>39</td>
</tr>
<tr>
<td>Chitosan</td>
<td>20.49</td>
<td>-</td>
<td>303</td>
<td>18</td>
</tr>
</tbody>
</table>

Comparison with other studies

The maximum adsorption capacity of 4-CP by activated carbon in this study was 47.6 mg/g. This value has been compared with \( q_m \) obtained in the literature for activated carbons prepared from various agricultural and industrial wastes (Table 3). It can be observed in table 3 that the activated carbon prepared from Aloe vera green waste can be considered as an effective adsorbent for uptake of 4-CP from aqueous media.

Conclusion

In this batch study, Aloe vera green waste activated carbon was used as an adsorbent for the uptake of 4-CP from aqueous solutions. The optimum contact time for the removal of 4-CP by carbon was 40 minutes. Moreover, the optimum pH acquired was 2. The Freundlich isotherm model and pseudo-second order kinetic model described the data better than other isotherm and kinetic models. It can be concluded from this study that Aloe vera green waste-based activated carbon can be employed as a low-cost adsorbent for the removal of 4-CP from aqueous solution.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

The author appreciates the financial support of this research by the Vice Chancellery for Research of Lorestan University of Medical Sciences.

References