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RESEARCH ARTICLE

# Adsorption of 2,4-dichlorophenoxyacetic acid on peanut shells: effect of initial concentration

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## ABSTRACT

Pesticides are an integral part of modern agriculture in most countries as a tool for controlling pests. In the last few decades, increasing use of pesticides is polluting environment and water resources day by day. Adsorption is one of the most used method for removal of these pollutions due to the simple ease of processing, low cost and effective even in very low concentrations. Active carbon is very efficient adsorbent for removing pesticides from aqueous solutions thanks to its high surface area and porosity. However, the high cost of active carbon can be sometimes restricted for several purposes.
In recent years, research on the production of low cost adsorbents alternative to commercially available activated carbon has increased. Therefore, in this work, peanut shells were used as an adsorbent for removing 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions. The adsorption performance was studied depending on initial concentrations of 2,4-D solutions.

***Keywords:*** Pesticide, adsorption, peanut shell, low-cost adsorbent

## 1. INTRODUCTION

Water pollution by chemical pollutants has become a primary public concern in the recent years. Among these pollutants, increasing use of pesticides in agriculture, forestry, and domestic activities for controlling pests is the major organic compound caused the water pollution. They are carcinogenic in nature and toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment [1, 2]. 2,4-Dichlorophenoxyacetic acid, more commonly referred to as 2,4-D, is member of the phenoxy family of pesticides. This pesticide is commonly used in the world to control broad-leaved weeds and pests in farm because of its low-cost and good selectivity. The maximum concentration of 2,4-D must be 20 mg $L^{-1}$ in drinking water based on the World Health Organization regulation [3]. Therefore, different processes have been used for the removal of these pesticides, such as enhanced electrochemical oxidation [4], photo degradation [5], oxidation by ozone [6] and adsorption [7-11].

Adsorption process is the most widespread treatment used due to the high removal efficiency and activated carbons are usually favored adsorbents based on their adsorption performance. However, the high cost of activated carbon had led to interest in utilizing low cost materials as adsorbents for pollutants. Therefore, in the present study, peanut shells were used as low-cost adsorbent for removal of 2,4-D from aqueous solutions. The equilibrium and kinetics of the adsorption process were studied to understand the adsorption mechanism of this pesticide onto the peanut shells.

## 2. MATERIALS AND METHODS

### *2.1. Adsorbent and Pesticide*

Peanut shells were used as low-cost adsorbent for removal of pesticide 2,4-D from aqueous solutions. Peanut shells are consisted of lignin, cellulose, and hemicellulose. The percentages of these components are determined as approximately 31% lignin, 36% cellulose and 19% hemicellulose [12]. Peanut shells

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were obtained from a local supplier in İstanbul. For experimental studies, the peanut shells were rinsed with tap water, then washed with distilled water dried at 80 °C in a hot air oven for 24 h, ground and then sieved to sizes of −50 and + 100 mesh. The powder was preserved in airtight bottles for experimental use.

2,4-D was purchased from Sigma Aldrich. The chemical formula of 2,4-D is $C_8H_6Cl_2O_3$ and its chemical structure was shown in Fig 1.

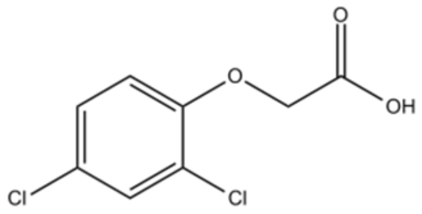

**Fig 1.** Chemical structure of 2,4-D

### 2.2. Equilibrium Experiments

The equilibrium adsorption experiments were performed to evaluate the efficiency of peanut shells for the removal of 2,4-D from aqueous solution. The experiments were carried out by adding 1 g of adsorbent into a set of 100 mL of different initial concentrations (10–50 mg L$^{-1}$) of 2,4-D solution. The samples were kept at constant temperature in an incubator shaker at 170 rpm and 25 °C for 3 h. The solutions were then centrifuged and the filtrate was analyzed using UV/vis spectrophotometer at 282 nm.

The equilibrium amount of 2,4-D adsorbed per unit mass of adsorbent, $q_e$ (mg g$^{-1}$), was calculated by:

$$q_e = \frac{(C_0 - C_e).V}{m} \quad (1)$$

where, $C_0$ and $C_e$ are the initial and equilibrium concentrations of 2,4-D (mg L$^{-1}$), respectively. $V$ is the volume of the solutions (L) and $m$ is the weight of adsorbent (g).

### 2.3. Kinetic Experiments

For kinetic studies, 1 g of peanut shell was contacted with a set of 100 ml of 2,4-D solutions with constant concentration. At a given time intervals, solutions were centrifuged and analyzed by UV/vis spectrophotometers for the residual concentration of 2,4-D. The amount of 2,4-D adsorbed at any time, $q_t$ (mg g$^{-1}$), was computed by:

$$q_t = \frac{(C_0 - C_t).V}{m} \quad (2)$$

where $C_t$ is the concentration of 2,4-D at any time (mg L$^{-1}$).

### 2.4. Adsorption Isotherm Models

Langmuir, Freundlich and Temkin isotherm models were used to evaluate the data obtained from the 2,4-D adsorption experiments:

*Langmuir model:*

$$\frac{1}{q_e} = \frac{1}{Q * b * C_e} + \frac{1}{Q} \quad (3)$$

where $q_e$ is the equilibrium adsorbed concentration (mg g$^{-1}$), $C_e$ is the equilibrium concentration (mg L$^{-1}$), $Q$ is the maximum sorption capacity (mg g$^{-1}$) and $b$ is the adsorption equilibrium constant.

*Freundlich model:*

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \quad (4)$$

where $K_f$ is the Freundlich affinity coefficient, $n$ is the Freundlich exponential coefficient.

*Temkin model:*

$$q_e = \frac{RT}{b_T} lnA_T + \frac{RT}{b_T} lnC_e \quad (5)$$

where $A_T$ and $b_T$ are the Temkin coefficients.

### 2.5. Adsorption Kinetics

Several methods are available to study the adsorption mechanism. In this study, in order to determine the adsorption kinetics, the data obtained from the 2,4-D adsorption process were analyzed with the pseudo first order, pseudo second order, Elovich and intra particle diffusion models.

*Pseudo first order model:*

$$ln(q_e - q_t) = k_1 t + ln(q_e) \quad (6)$$

where; $q_e$ is the adsorbed amount at equilibrium (mg g$^{-1}$), $q_t$ is the adsorbed amount at time $t$ (mg g$^{-1}$), and $k_1$ is the rate constant (min$^{-1}$).

*Pseudo second order model:*

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where, $k_2$ is the pseudo second order adsorption kinetic parameter (g mg$^{-1}$ min$^{-1}$).

*Elovich model:*

The Elovich equation is valid for chemisorptions kinetics and systems in which the surface is heterogeneous.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (8)$$

where; $\alpha$ is the initial adsorption rate (mg g$^{-1}$ min$^{-1}$), $\beta$ is the constant related to extent of surface coverage and activation energy consumption (g mg$^{-1}$).

*Intra particle diffusion model:*

$$q_t = k_i t^{0.5} + C_i \quad (9)$$

where; $k_i$ is the intra particle diffusion kinetic parameter (mg g$^{-1}$ min$^{-2}$), and $C_i$ is the constant related to layer thickness (mg g$^{-1}$).

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Initial Concentration

In order to determine the effect of initial concentration of 2,4-D, the adsorption of this pesticide on peanut shell adsorbent at constant pH and temperature value was studied as a function of different initial concentrations and the results were shown in Fig 2.

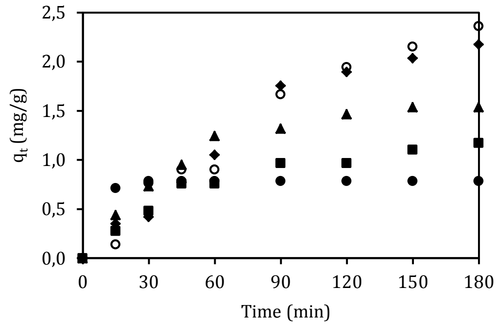


**Fig 2.** Effect of initial concentration on the adsorption of 2,4-D on peanut shells (● 10 mg $L^{-1}$; ■ 20 mg $L^{-1}$; ▲ 30 mg $L^{-1}$; ♦ 40 mg $L^{-1}$; ○ 50 mg $L^{-1}$)

### 3.2. Adsorption Isotherms

Three classic adsorption models (Langmuir, Freundlich and Temkin isotherm models) were used to describe the equilibrium adsorption data of the 2,4-D onto peanut shell samples.

The % removal value decreased from 78.6 to 47.2 as the initial concentration was increased from 10 to 50 mg $L^{-1}$; indicating the effect of loading of pesticides molecules on adsorption. However, the total amount of 2,4-D adsorbed on the adsorbent increases with increase in 2,4-D concentration in the initial solution. It is clear that the rate of adsorption of both the pesticides depends on the initial concentration of pesticides.

Among these isotherm models, Freundlich isotherm model was determined as the most appropriate one for the pesticide adsorption data with the high values of correlation coefficient ($R^2$) and low values of standard error (δ). The statistical parameters of these models were presented in Table 1. $K_f$ and $n$ were Freundlich coefficients which show the capacity of adsorption and adsorption intensity, respectively. The adsorption intensity, $n$, represents the degree of non-linearity between solution concentration and adsorption. If $n$<1 then adsorption is chemical adsorption; if $n$>1 then adsorption process is physical [13]. From Table 1, the $K_f$ and $n$ were found as 0.5231 and 2.40, respectively. This $n$ value (2.40) indicates the physical adsorption of pesticide onto peanut shell. The situation $n$>1 is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density [13]. This result ($n$>1) was in agreement with the results obtained from literature for adsorption of Tartrazine using hen feathers [14], adsorption of zinc ions using coal fly ash [15].

### 3.3. Adsorption Kinetic Modelling

Evaluation of the adsorption kinetic as well as adsorption equilibrium is very important to plan and control the adsorption process. In order to describe the adsorption kinetic, the pseudo first order, the pseudo second order, Elovich and the intra particle diffusion models were used for the evaluation of kinetic data obtained from the adsorption experiments. As can be seen from Table 2, among these models, pseudo first order kinetic model was observed as the most appropriate one for all the experimental data with the high values for the coefficient of determination and low the standard error values. According to Table 2, the rate constant, $k_1$, was found as 0.0143 $min^{-1}$ for adsorption of 2,4-D pesticide onto peanut shell. Similar kinetic model was found from literature for adsorption of acid dyes onto chitosan [16], adsorption of N719 dye on $TiO_2$ surface [17] and adsorption of Cr(VI) onto hazelnut shell activated carbon [18].

**Table 1.** The estimated parameters and statistical values of isotherm models for 2,4-D adsorption onto peanut shell samples

| Adsorption Isotherm | Isotherm Equations | R² | δ |
|---|---|---|---|
| **Langmuir** | $C_e/q_e$= 0.3143$C_e$ + 3.6618 | 0.8194 | 1.4231 |
| **Freundlich** | ln($q_e$)=0.416ln($C_e$)–0.6479 | 0.9347 | 0.1368 |
| **Temkin** | $q_e$ = 0.6269ln($C_e$) – 0.0624 | 0.8160 | 0.2999 |

**Table 2.** The estimated parameters and statistical values of kinetic models for 2,4-D adsorption onto peanut shell samples

| Kinetic Model | Model Equations | R² | δ |
|---|---|---|---|
| **Pseudo First Order** | $ln(q_e$-$q_t)$ = 0.0143$t$ + 0.907 | 0.9902 | 0.1061 |
| **Pseudo Second Order** | $q_t/t$ = 0.2416$t$ + 33.087 | 0.9701 | 2.7162 |
| **Elovich** | $q_t$ = 0.8063ln$t$ -1.9364 | 0.9672 | 0.6542 |
| **Intra Particle Diffusion** | ln$q_t$ = 0.6851ln$t$ – 2.6362 | 0.9895 | 0.7819 |

## 4. CONCLUSION

Adsorption experiments were carried out using adsorption equilibrium and kinetics to investigate the adsorption ability of the peanut shell samples. The amount of 2,4-D adsorbed increased with increasing 2,4-D concentration in the initial solution. The isotherm data for 2,4-D adsorption on peanut shell fitted well to the Freundlich isotherm model. Furthermore, kinetic data were fitted to the pseudo-first-order kinetic model. As a result, it can be concluded that peanut shell samples can be employed as effective adsorbents for adsorption of pesticides.

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