Batch Adsorber Design for Different Solution Volume/Adsorbate Mass Ratios of Bentazon, Carbofuran and 2,4-D Adsorption on to Date Seeds Activated Carbon

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Abstract

The Adsorption isotherms and equilibrium of bentazon, carbofuran and 2,4-Dichlorophenoxyacetic acid (2,4-D) onto date seeds activated carbon (DSAC) were examined in batch process. Adsorption studies were conducted in the pesticides initial concentrations range of 25–250 mg/L and temperature of 30 °C. The experimental equilibrium data were analyzed by non-linear fitting using Langmuir, Freundlich and Temkin isotherm models. Equilibrium data fitted better with the Langmuir model showing maximum monolayer adsorption capacity of 78.13, 135.14 and 175.4 mg/g, for bentazon, carbofuran and 2,4-D respectively onto DSAC. A single stage batch absorber was designed for different operating line (V/M) ratios. Equilibrium data were obtained from the Langmuir isotherm at different V/M ratios using the mass balance equation for the batch absorber system. A simple linear expression relating the parameters involved in the batch absorber design was proposed for the studied system.

Keywords: Bentazon; Carbofuran; 2,4-D; Adsorption; Isotherm models; Batch absorber design

Introduction

Pesticides are indispensable in modern agriculture, but their use and/or misuse may lead to serious deterioration in water quality which could impair the use of water for purposes of crop protection, animal production or even human consumption [1,2].

Bentazon is a newly emerging herbicide used for selective control of broadleaf weeds and sedges in beans, rice, corn, peanuts, and mint. It is one of the most commonly used herbicides in agriculture and gardening. However, through leaching or run-off from agricultural lands, deposition from aerial applications and indiscriminate discharge of industrial wastewaters, bentazon has become a reckoned source of contaminant to water resources with its attendant threats to the ecosystem and environment in general; the maximum allowable concentration is 0.05 mg/L in tap water [3-7].

Carbofuran is a broad spectrum systemic acaricide, insecticide and nematicide included in the general group of the carbamate derivative pesticides. It is widely used for the control of soil dwelling and foliar feeding insects including wireworms, white grubs, stem borers, aphids and several other insects. The maximum acceptable concentration (MAC) for carbofuran in drinking water is 0.09 mg/L [7-12].

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the oldest herbicides used in the world, 2,4-D is a selective herbicide that kills dicots (but not grasses) by mimicking the growth hormone auxin, which causes uncontrolled growth and eventually death in susceptible plants. It is considered as moderately toxic and maximum allowable concentration is 0.1 mg/l in drinking water [13-20].

Adsorption techniques have gained popularity recently due to their efficiency in the removal of pollutants; in addition adsorption produces high quality products and is an economically feasible process [21,22]. Adsorption is considered to be superior compared to other techniques due to its low cost, availability, simplicity of design, high efficiency, ease of operation biodegradability and ability to treat pollutants in more concentrated form [12]. Besides, adsorption does not result in the formation of harmful substances [15]. Adsorption onto activated carbon is one of the most promising techniques for pesticide removal due to flexibility in design and operation [18]. Pits of date palm (seeds) are waste products which were used as precursors for preparation of mesoporous activated carbon [20-23].

The effect of volume of solution to the adsorbent mass ratio (V/M) on the equilibrium uptake of pesticide solution at different initial concentrations is an important factor to be considered in adsorber design. However, this requires an extensive experimental work to determine the isotherm parameters for different V/M ratios and also at different initial pesticide concentrations. In this study a single stage batch absorber was designed for different V/M ratio of bentazon solutions on date seeds activated carbon using the experimental equilibrium data obtained at a single V/M ratio.

In this study a single stage batch absorber was achieved. The design objective is to reduce the pesticide solution of volume V (L) from the initial concentration of Co to C1 (mg/L). The amount of adsorbent is M (g) and the solute loading changes from q0 to q1 (mg/g). At the time t = 0, qo = 0 and as time proceeds the mass balance equates the pesticides removed from the liquid to that picked up by the solid [1,23].

Materials and Methods

Pesticides

Bentazon, carbofuran and 2,4-D were obtained from Sigma–Aldrich (M) Sdn. Bhd., Malaysia and were used as adsorbate. It was of analytical grade and was used without further purification. Distilled water was used in the preparation of all solutions. Some properties and chemical structures of the bentazon herbicide are given in Table 1.
Preparation and characterization of activated carbon

Date fruits seeds (DS) used for preparation of activated carbon. The procedure used to prepare the activated carbon was referred to our previous work [4]. The raw material, DS was collected, firstly washed with distilled water to remove all dirt and then oven dried overnight at 105°C. The dried pits were then crushed to desired mesh size (1–4 mm). The process of converting DS to AC comprises of two stages: carbonization and activation. Both carbonization and activation were carried out in a stainless steel vertical tubular reactor placed in a tube furnace. The dried DS were placed on a stainless steel sampling cylinder inside the reactor, then heated at a rate of 10°C /min to 700°C and held at this temperature for 2 h in a N2 atmosphere. The carbonized material was then soaked in 6M potassium hydroxide (KOH) solution with impregnation ratio (KOH: char) of 3.75 (w/w). The mixture was then dehydrated in an oven overnight at 105°C to remove moisture and then activated under the same conditions as carbonization, but to activation temperature of 850°C. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide (CO2) and activation was held for 3 h and 37 min. The CO2 was used as the gasifying agent for the improvement of the porosity of the AC produced. The resulting AC was washed with 0.1 M HCl to dissolve and remove any residual ash followed by washing with hot distilled water to regulate the pH around 7 and finally drying overnight at 70°C.

Batch adsorption equilibrium studies

The adsorption experiments of pesticides onto DSAC were carried out in a set of 250 mL Erlenmeyer flasks 200 mL of the pesticides solutions of various initial concentrations in the range 25–250 mg/L. Equal mass of 0.20 g of the prepared activated carbon with particle size of (200 –300 µm) was added to each flask and kept in an isothermal shaker of 120 rpm at 30°C for 30 h to reach equilibrium. The pH of the solutions was original without any pH adjustment.

Aqueous samples were taken from each of the pesticides solutions at preset time intervals using disposable syringes and the concentrations were then analyzed. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of pesticides in the supernatant solution before and after adsorption were determined using a double beam UV–visible spectrophotometer (UV-1700 Shimadzu, Japan) at 333, 273 and 283 nm for bentazon, carbofuran and 2,4-D, respectively.

The amount of adsorption at equilibrium, qe (mg/g), was:

\[ q_e = \frac{(C_o - C_e)V}{W} \]

where \( C_o \) and \( C_e \) (mg/L) are the liquid phase concentrations of pesticide at the initial and equilibrium conditions, respectively. \( V \) (L) is the volume of the solution and \( W \) (g) is the mass of DSAC.

Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [24]. The linear form of Langmuir isotherm equation is given as:

\[ \frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} \]

where \( C_e \) is the equilibrium concentration (mg/L); \( q_e \) the amount pesticides adsorbed at equilibrium (mg/g); \( q_m \) the adsorption for complete monolayer (mg/g); \( K_a \) is the sorption equilibrium constant (L/mg).

The essential characteristic of the Langmuir isotherm is defined by Weber and Chakkravorti as:

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

where \( b \) (L/mg ) is the Langmuir constant and \( C_o \) (mg/L) is the adsorbate initial concentration. The parameter \( R_L \) indicates the nature of the adsorption process as explained in Table 2.
Freundlich isotherm

Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [24,25]. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( q_e \) is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), \( K_F \) and \( n \) are Freundlich constants with \( n \) giving an indication of how favorable the adsorption process. \( K_F \) (mg/g (l/mg)^1) is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of herbicide adsorbed onto activated carbon for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption.

Temkin isotherm

Temkin and Pyzhov [26] considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The Temkin isotherm has been used in the form as follows:

\[
q_e = B \ln A + B \ln C_e
\]

where \( B = RT/b \), \( b \) is the Temkin constant related to heat of sorption (J/mol); \( A \) is the Temkin isotherm constant (L/g), \( R \) the gas constant (8.314 J/mol K) and \( T \) the absolute temperature (K).

Results and Discussion

Effect of contact time and initial concentration on adsorption equilibrium

The adsorption uptake at equilibrium was found to increase with an increase in the initial pesticides concentration. This was because when the initial concentration increased; the mass transfer driving force would become larger consequently resulting in higher pesticide adsorption.

Figure 1a show that the contact times needed for bentazon solutions with initial concentrations of 25-50 mg/L to reach equilibrium on DSAC was around 5 h, and for the concentrations of 100-200 mg/L, 25-27 h was required, while for bentazon solutions of higher initial concentration 250 mg/L equilibrium time of 34-36 h was required.

For the case of adsorption of carbofuran on to DSAC, the adsorption capacity at various carbofuran initial concentration of 25-250 mg/L, the amount of carbofuran adsorbed, \( q_t \) increased in a similar pattern to bentazon pesticide adsorption on DSAC surface. The adsorption uptake at equilibrium was found to increase with an increase in the initial insecticide concentration as appear in Figure 1-b, which shows that longer contact times were required to reach equilibrium by the carbofuran solutions of higher initial concentrations. The contact time needed for carbofuran solutions with initial concentration of 25-100 mg/L to reach equilibrium on DSAC was around 4-5h, and for higher initial concentrations (150-250 mg/L) an equilibrium time of 14-16 h was required.

For the case of adsorption 2,4-D pesticide on DSAC, the adsorption uptake at various 2,4-D initial concentration of (25-250 mg/L) at 30 oC were as shown in Figure 1-c. It is clear from this Figure that the amount of 2,4-D adsorbed, \( q_t \) increased with time. The equilibrium adsorption was achieved in 5-7 h for 2,4-D solution with initial concertinos of 50-200 mg/L and 11-14 h for 250-300 mg/L to reach equilibrium.

Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the pesticides species between the liquid phase and the solid phase when the adsorption process reaches equilibrium state. The experimental data obtained in this study were fitted to the three most commonly used isotherm models: Langmuir, Freundlich and Temkin models. The adsorption isotherm parameters values obtained for adsorption of bentazon, carbofuran and 2,4-D onto DSAC at 30 oC are listed in Table 3.

Based on the correlation coefficient, \( R^2 \) listed in Table 3 it can be concluded that the adsorption of bentazon onto DSAC at 30 oC was demonstrated well by both of Langmuir and Freundlich isotherm models. The correlation coefficient, \( R^2 \) for both models was 0.925 ≤ \( R^2 \).
amount of adsorbent is $M$ (g) and the solute loading changes from $q_e$ to $q_o$ (mg/g). At the time $t = 0$, $q_e = 0$ and as time proceeds the mass balance equates the pesticides removed from the liquid to that picked up by the solid [23].

The mass balance equation for the sorption system in Figure 2 can be written as:

$$V (C_i - C_e) = M (q_e - q_i) = M q_e$$  \hspace{1cm} (6)

At equilibrium conditions; \hspace{1cm} $C_1 \rightarrow C_e$ and $q_i \rightarrow q_e$  \hspace{1cm} (7)

Since the sorption isotherm studies confirm that the equilibrium data for pesticides onto DSAC fitted well in Langmuir isotherm, Langmuir isotherm equation can be used for $q_e$ in equation batch absorber design.

Equation (6) can be rearranged as:

$$\frac{M}{V} (C_i - C_e) = \frac{q_e}{q_i} - \frac{q_e}{q_o} = q_e (K_e C_1^{1/n} + 1)$$  \hspace{1cm} (8)

Figure 3 show the plot between the predicted amounts of activated carbon prepared as adsorbent for bentazon removal at initial concentration of 50 mg/L for different percentage removal and solution volume at 30ºC.

From this Figure the amount of the adsorbent (DSAC) used with pesticides in this study can detect with the range of pesticides removal (60-90%) and solution volume range of 2–16 L.

Also this Fig. can be extended to include other values of pesticides removals till 100%, and can be modification to include any other conditions from initial concentration and solution temperature.

### Table 3: Isotherm model parameters and correlation coefficients for adsorption of bentazon, carbofuran and 2,4-D onto DSAC at 30 °C.

| Isotherm models | Parameters |
|-----------------|------------|
| Bentazon onto DSAC | $q_e$ (mg/g) | $b$ (L/mg) | $R^2$ |
| Langmuir       | 78.13      | 0.061 | 0.925 |
| Freundlich     | 12.48      | 0.405 | 0.960 |
| Temkin         | 1.18       | 13.75 | 0.890 |
| Carbofuran onto DSAC | $q_e$ (mg/g) | $b$ (L/mg) | $R^2$ |
| Langmuir       | 135.14     | 0.041 | 0.960 |
| Freundlich     | 10.47      | 0.546 | 0.934 |
| Temkin         | 5.05       | 29.28 | 0.975 |
| 2,4-D onto DSAC | $q_e$ (mg/g) | $b$ (L/mg) | $R^2$ |
| Langmuir       | 175.4      | 0.036 | 0.898 |
| Freundlich     | 19.32      | 0.433 | 0.952 |
| Temkin         | 5.05       | 29.28 | 0.975 |

**Figure 2:** Single stage batch absorber design.
Conclusion

The present study shows that the DSAC proved to be an effective adsorbent for removing bentazon, carbofuran and 2,4-D from aqueous solutions. The equilibrium data were best described by the Langmuir and Freundlich isotherm model. A single stage batch adsorber was designed for different V/M ratios of pesticides and activated carbon selected using the experimental equilibrium data obtained at a single V/M ratio.

References

1. Salman JM (2013) Preparation of activated carbons for adsorption of pesticides. LAP Lambert Academic Publishing.
2. Salman JM (2014) Preparation of Banana Bunch Fruits Activated Carbon for Pesticides Removal from Aqueous Solution. Progress in Chemical Engineering 1: 19-21.
3. Salman JM (2014) Optimization of preparation conditions for activated carbon from palm oil fronds using response surface methodology on removal of pesticides from aqueous solution. Arabian Journal of Chemistry 7:101–108.
4. Salman JM, Abid FM (2013) Preparation of mesoporous activated carbon from palm-date pits: Optimization study on removal of bentazon, carbofuran and 2,4-D using response surface methodology. Water Sci Technol 68: 1503–1511.
5. Salman JM, Saad KA (2012) Batch study for herbicide bentazon adsorption onto palm oil fronds activated carbon. J Chem Sci 10: 731-740.
6. Ayanci E, Hoda N (2004) Adsorption of bentazon and propanil from aqueous solutions at the high area activated carbon-cloth. Chemosphere 57: 755-762.
7. Salman JM, Hameed BH (2010) Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions. J Hazard Mater 175: 133-137.
8. Salman JM, Mohammed JM (2013) Batch study for herbicide bentazon adsorption onto branches of pomegranates trees activated carbon. Desalination and Water Treatment Journal 51: 5005-5008.
9. Salman JM, Njoku VO, Hameed BH (2011) Bentazon and carbofuran adsorption onto date seed activated carbon: Kinetics and equilibrium. Chemical Engineering Journal 173: 361-368.
10. Salman JM, Hameed BH (2010) Removal of insecticide carbofuran from aqueous solution by banana stalks activated carbon. J Hazard Mater 175: 133–137.
11. Salman JM, Njoku VO, Hameed BH (2011) Adsorption of pesticides from aqueous solution onto banana stalk activated carbon. Chemical Engineering Journal 174: 41-48.
12. Salman JM, ABD FM, Muhammed AA (2011) Adsorption of herbicide insecticide from aqueous solution using commercial activated carbon. Int J Chem Sci 9: 557-564.
13. Benitez FJ, Acero JL, Real FJ (2002) Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes. J Hazard Mater 89: 51-65.
14. Salman JM, Mahmoud WA, Muhammed AA, Abid FM (2012) Adsorption study of carbofuran onto mesoporous activated carbon prepared from palm oil fronds. Int J Chem Sci 10: 768-776.
15. Salman JM, Njoku VO, Hameed BH (2011) Batch and fixed-bed adsorption of 2,4-dichlorophenoxyacetic acid onto oil palm frond activated carbon. Chemical Engineering Journal 174: 33-40.
16. Ayar N, Bilgin B, Atun G (2008) Kinetics and equilibrium studies of the herbicide 2, 4-dichlorophenoxyacetic acid adsorption on bituminous shale. Chemical Engineering Journal 138: 239-248.
17. Salman JM, Saad KA (2012) Adsorption of 2,4-D onto date seeds activated carbon: Equilibrium, kinetic and thermodynamic studies. Int J Chem Sci 10: 677-690.
18. Aksu Z, Kabasakal E (2004) Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon. Separation and Purification Technology 35: 223-240.
19. Salman JM (2011) Batch and fixed-bed adsorption studies of 2,4-D pesticide from aqueous solution using coconut activated carbon. Int J Chem Sci 9: 620-626.
20. Fytianos K, Voudrias E, Kokkalis E (2000) Sorption–desorption behavior of 2,4-dichlorophenol by marine sediments. Chemosphere 40: 3-6.
21. Salman JM, Hameed BH (2010) Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. Desalination 256: 129–135.
22. Salman JM, Hameed BH, Ahmad AL (2009) Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones. J Hazard Mater 163: 121-126.
23. Kumar KV, Porkodi K (2007) Batch adsorber design for different solution volume/adsorbent mass ratios using the experimental equilibrium data with fixed solution volume/adsorbent mass ratio of malachite green onto orange peel. Dyes and Pigments 74: 590 – 594.
24. Langmuir I (1918) The adsorption of gases on plan surfaces of glass, mica and platinum. Journal of American Chemical Society 40: 1361-1403.
25. Freundlich HMF (1906) Over the adsorption in solution. J phys chem.
26. Temkin MI, Pyzhev V (1940) Kinetics of ammonia synthesis on promoted iron catalyst. Acta Physiochemical USSR 12: 327-356.