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BATCH AND FIXED-BED ADSORPTION STUDIES OF 2,4-DICHLOROPHENOXYACETIC ACID PESTICIDE FROM AQUEOUS SOLUTION USING COCONUT ACTIVATED CARBON

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ABSTRACT

Adsorption study of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution using commercial coconut activated carbon (CAC) as adsorbent has been carried out in batch experiments revealed that the equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherm models and were found to be best represented by the Langmuir isotherm model; with maximum monolayer adsorption capacity of 300 mg/g at 30°C when the initial concentration was 50–300 mg/L. At the same time a fixed-bed adsorption study of 2,4-D from aqueous solution using CAC as adsorbent has been achieved using fixed-bed column where the effects of important factors such as the initial 2,4-D concentration, flow rate and bed height on the breakthrough characteristics of the adsorption system were evaluated. The results obtained confirmed that the breakthrough curves were dependent on initial pesticide concentrations, flow rate and bed height with the highest bed capacity of 50 mg/g at 150 mg/L initial 2, 4-D concentration, 10 mL/min flow rate and.3 mm bed height

Key words: Adsorption, 2,4-D, Activated carbon, Isotherm, Batch process, Continuous process.

INTRODUCTION

Pesticides may be of the board spectrum type which kills a wide range of organisms or the selective type which destroys one organism or few specific organisms[1]. The herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D) is most extensively applied to control broad-leaved weeds and pests in fields worldwide. 2,4-D are widely used pesticides found in surface and ground water in the world. By the World Health Organization (WHO) drinking water quality standard is 0.20 mg/ L for 2-4 D[2,3].

Several methods either independent or in conjunction have been used for the removal

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of these pesticides including chemical oxidation with ozone[4], photodegradation[5], combined ozone and UV irradiation[6], Fenton degradation[7], biological degradation[8], ozonation[9], membrane[10] and adsorption[11].

Adsorption has been widely used to remove toxic compounds from polluted waters; this technology is presently the most viable option being employed for the removal of such pesticides from wastewaters[2].

EXPERIMENTAL

Material and methods

Pesticide and activated carbon

Technical grade 2,4-D supplied by Sigma-Aldrich was used as an adsorbate. Distilled water was used to prepare all solutions. Commercial coconut activated carbon (CAC) used in this study.

Batch equilibrium studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 100 mL of 2,4-D solutions with initial concentrations of 100-300 mg/L were placed in these flasks. Equal amount of 0.3 g of activated carbon was added to each flask and kept in an isothermal (30°C) shaker at 120 rpm for 15 h to reach equilibrium. At intervals of time, samples were taken from the solution and the concentrations determined. All samples were filtered prior to the analysis in order to minimize the interference of carbon fines present in solution. The concentrations of 2,4-D in the supernatant solution before and after adsorption were determined using a double beam UV-visible spectrophotometer (Shimadzu 1700, Japan) at 284 nm. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by -

$$q_e = \frac{(C_o - C_e)V}{W} \quad \ldots(1)$$

Where C_0 and C_e (mg/L) are the liquid phase concentrations of 2,4-D at the initial and equilibrium conditions, respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used.

Adsorption isotherm

Three isotherm models (Langmuir, Freundlich and Timken) were used to test the fitting of the experimental data. The linear form of Langmuir isotherm equation[12] is given as-

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad \ldots(2)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_m (mg/g) is a monolayer adsorption capacity, and b(L/mg) is the equilibrium adsorption constant. The linear form of Freundlich[13] isotherm is given by the following equation -

$$\log q_e = \ln K_F + \left(\frac{1}{\boldsymbol{n}}\right) \log C_e \qquad \ldots(3)$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, K_F (mg/g (l/mg)$^{1/n}$) and n are Freundlich constants. In the case of, Timken isotherm[14], it is used in the form given below.

$$q_e = \mathrm{B} \ln\mathrm{A} + \mathrm{B} \ln \mathrm{Ce} \qquad \ldots(4)$$

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

Column studies

The experimental set up for the fixed bed adsorption process is comprised of by a stirred feed tank, peristaltic pump (Masterflex, Cole-Parmer Instrument C_o), an adsorption glass column made of Pyrex glass tube of 120 mm inner diameter and 18 mm height. A stainless sieve was attached to the bottom of the column followed by a layer of glass wool. The column was then filled up with 5 mm size glass beads in order to provide a uniform flow of the solution through the column. 2.5 g of CAC used as adsorbent in the column, 2,4-D solution of known concentration 100 mg/L was pumped upward through the column at a desired flow rate of 10 mL/min controlled by a peristaltic pump. The pesticide solution at the outlet of the column were then collected at regular time interval for analysis using a double beam UV-visible spectrophotometer to determine the concentrations.

RESULTS AND DISCUSSION

Effect of contact time and initial 2,4-D concentration on adsorption equilibrium

Fig. 1 shows the 2,4-D adsorption uptake with time for various initial 2,4-D concentrations at 30°C. It indicates that the contact time needed for 2,4-D solutions with initial concentrations of 100 mg/L to reach equilibrium was less than 100 min. For 2,4-D solutions with initial concentrations of 200-300 mg/L, equilibrium time of 300 min was required. As would be observed from Fig. 1, the amount of 2,4-D adsorbed onto the surface of activated carbon increased with time.

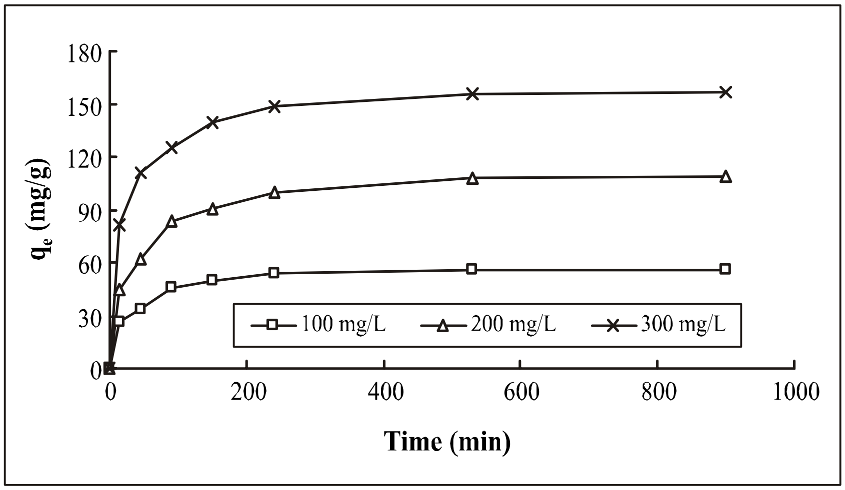

Fig. 1: Adsorption capacity with contact time of various intial concentration of 2,4-D onto CAC

Adsorption isotherms

The Langmuir, Freundlich and the Temkin isotherms were used to describe the experimental results. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Figures not shown) gave the Langmuir constant, q_m and R^2, which were determined from the slope and intercept of the plot and are presented in Table 1. Similarly, the values of K_F and n for Freundlich isotherm were calculated from the intercept and slope of equation 3 are given in Table 1 and the constants *A* and *B* of Temkin isotherm described by equation 4 above are also presented in Table 1. As would be observed from Table 1, the monolayer adsorption capacity according to Langmuir is model is 300 mg/g for 2,4-D. The correlation coefficient (R^2), which describes the fitness of a set of data revealed that Langmuir isotherm best describes the adsorption of the considered pesticides than the others with R^2 of 0.999 for 2.4-D. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto CAC surface.

Table 1: Lungmiur, Frendulich and Temkin results

Langmuir isotherm	Value
q_m (mg/g)	300
b (L./mg)	0.0132
R^2	0.999
Freundlich isotherm	
n	1.4
K_F [(mg /g)(L./mg)$^{1/n}$]	8.35
R^2	0.997
Temkin isotherm	
A (L/g)	1.9
B (J/mol)	68.7
R^2	0.991

Effect of initial concentration for column study

The effect of the initial 2,4-D concentration of 100 mg/L with the adsorbent bed height of 30 mm and pesticide solution flow rate of 10 mL/min were studied. Fig. 2 show the breakthrough curve for adsoption of 2,4-D onto coconut activated carbon at initial concentration of 100 mg/L, flow rate of 10 mL/min and total weight of activated carbon of 2.5 g. The bed adsorption capacitiy for 2,4-D was 50 mg/g.

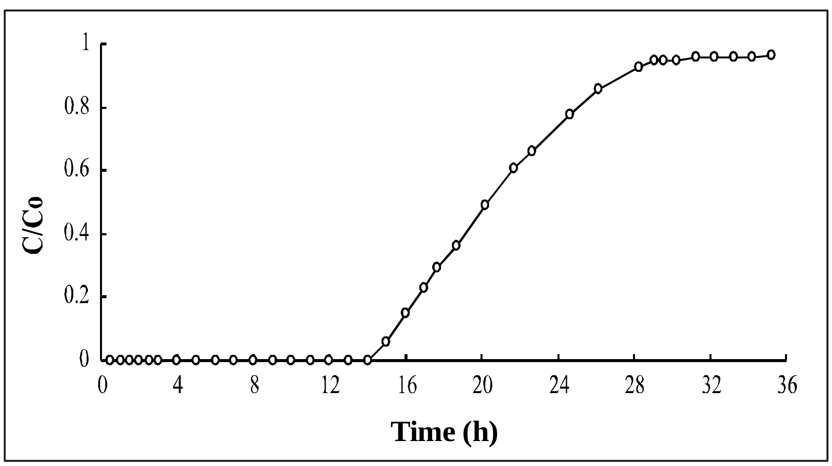

Fig. 2: Breakthrough curve for 2,4-D (100 mg/L and 10 mL/min) onto 2.5 g CAC

CONCLUSION

The present investigation showed that commercial coconut activated carbon is a promising adsorbent for the removal of 2,4-D from aqueous solutions. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by the Langmuir isotherm model; with a maximum monolayer adsorption capacity of 300 mg/g at 30°C for 2,4-D. A column experiment for this pesticide onto CAC shows that the adsorption bed capacity was 50 mg/g.

REFERENCES

1. Sahabat Alam, Malaysia, Pesticides Dilemma in the World, Phoenix Press Sdn. Bhd. Penang, Malaysia.
2. V. K. Gupta, I. Ali, Suhas and V. K. Saini, Adsorption of 2,4-D and Carbofuran Pesticides using Fertilizer and Steel Industry Wastes, J. Colloid Interface Sci., **299**, 556-563 (2006).
3. P. Skladal, G. S. Nunes, H. Yamanaka and M. L. Ribeiro, Detection of Carbamate Pesticides in Vegetable Samples using Cholinesterase-Based Biosensors, *Electroanalysis,* **9**, 1083-1087 (1997).
4. F. J. Beltrán, J. F. Garcia-Araya and B. Acedo, Advanced Oxidation of Atrazine in Water II : Ozonation Combined with Ultraviolet Radiation, Water Res., **28**, 21-53 (1994).
5. A. Zertal, M. Jacquet, B. Lavédrine and T. Sehili, Photodegradation of Chlorinated Pesticides Dispersed on Sand, Chemosphere, **58**, 1431-1437 (2005).
6. S. Malato, J. Blanco, C. Richter, B. Milow and M. I. Maldonado, Solar Photocatalytic Mineralization of Commercial Pesticides Methamidophos, Chemosphere, **38**, 1145-1156 (1999).
7. J. R. Watts and S. E. Dilly, Evaluation of Iron Catalysts for the Fenton-Like Remediation of Diesel-Contaminated Soils, J. Hazard. Mater, **51**, 209-224 (1996).
8. H. Chen, X. He, X. Rong, W. C. P. Cai, W. Liang, S. Li and Q. Huang, Adsorption and Biodegradation of Carbaryl on Montmorillonite, Kaolinite and Goethite, Applied Clay Science., **46**, 102-108 (2009).
9. W. Hua, E. R. Bennett and R. J. Letcher, Ozone Treatment and the Depletion of Detectable Pharmaceuticals and Atrazine Herbicide in Drinking Water Sourced from the Upper Detroit River, Ontario, Canada. Water Res., **40**, 2259-2266 (2006).

10. J. A. M. H. Hofman, E. F. Beerendonk, H. C. Flolmer and J. C. Kruithof, Removal of Pesticides and other Micropollutants with Cellulose-Acetate, Polyamide and Ultra-Low Pressure Reverse Osmosis Membranes, Desalination, **113**, 209-214 (1997).

11. N. Daneshvar, S. Aber, A. Khani and M. H. Rasoulifard, Investigation of Adsorption Kinetics and Isotherms of Imidacloprid as a Pollutant from Aqueous Solution by Adsorption Onto Industrial Granular Activated Carbon. J. Food Agriculture Environ., **5(3 & 4)**, 425-429 (2007).

12. I. Langmuir, The Adsorption of Gases On Plan Surfaces of Glass, Mica and Platinum, J.Am. Chem. Soc., **40**, 1361-1403 (1918).

13. H. Freundlich, Uber die Adsorption in Iosungen (Adsorption in solution), Z. Phys. Chem., **57**, 384-470 (1906).

14. M. J. Temkin and V. Pyzhev, Recent Modifications to Langmuir Isotherms, Acta Physiochim. URSS, **12**, 217-222 (1940).

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