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Removal of pesticide in agricultural runoff using granular-activated carbon: a simulation study using a fixed-bed column approach

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ABSTRACT

The use of pesticide and its subsequent release to the environment is a major concern for modern society as concerns over environmental pollution associated with toxic emission are recognized due to contaminants present in pesticide (particularly malathion). Adsorption process using activated carbon is among the most effective techniques for the removal of pesticides in the treatment of various waste streams. The adsorption of pesticide containing malathion in agricultural runoff was investigated using granular-activated carbon (GAC) as the adsorbent; GAC made of coconut, and palm shells were used and their effectiveness in retaining the pesticide is discussed. A fixed-bed column test was performed to simulate the actual condition of adsorption in a continuous manner in a filtration process. Different flow rates were used to evaluate their effects on the column performance, where different breakthrough curves were obtained. The Adam–Bohart breakthrough curve equation was used to predict the breakthrough curve and to obtain the adsorption capacity of pesticide on GAC. The results showed that the Adam–Bohart equation fitted the experimental data well, and the use of a bed of GAC as the adsorbent in the set up showed high capacity in retaining the pesticide present in the aqueous solution, achieving removal efficiency at the rate of 71.4 and 82.9% for palm shell activated carbon and coconut shell activated carbon, respectively. Our results indicate that the use of GAC through adsorption process shows exceptional promise as a means for treating problematic pesticide in agricultural runoff.

Keywords: Pesticide; Granular activated carbon; Adsorption; Malathion; Filtration

1. Introduction

The increased use of pesticides, such as herbicides and insecticides, in agriculture has made the removal of these harmful compounds from surface waters an important environmental protection issue [1]. There are many methods to treat raw water contaminated by harmful organics such as malathion. These include ozonization, oxidation, disinfection, photocatalysis, and removal by adsorption. The most commonly

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applied method is adsorption because of its efficiency, capacity, and applicability to large-scale operation. Adsorption on activated carbon is a well-established and effective technique for raw water treatment [2]. Malathion is an insecticide that always causes pollution on water system, and thus, many efforts have been made to treat the polluted water [3]. Malathion, (O,O dimethyl S-(1,2-dicarbethoxyethyl)phosphorodithioate), a chemical compound commonly referred to as organophosphorous insecticides, is frequently used for the control of insects on fruits and vegetables, and also to control mosquitoes, flies, miscellaneous household insects, animal parasites, and human head and body lice [4]. Malathion is nonsystemic and it kills insects by direct contact or through vapor action. It is the active ingredient in numerous pesticide formulations and is readily available at the local market. Malathion may be released into aquatic environment especially to the river through intentional application (e.g. control of aquatic weeds, algae, fish, or unwanted invertebrates), aerial drift, or runoff from agricultural application. This pollutant can be transferred to the atmosphere through volatilization, in addition to being transported by the flow of river that are directly linked to estuaries, coasts, and open seas [5].

Activated carbon is an adsorbent known with the strongest physical adsorption forces and the highest volume of adsorbing porosity of any material known to mankind [6]. It is produced from material such as almond, coconut shell, walnut hills, woods, and coal. Activated carbon can be versatile adsorbents that can be used in a wide range of applications, particularly for the removal of impurity species from the liquid or gas phase by adsorption [7]. Its application as a filter medium is diversified in potable water treatment because of its high adsorptive properties. The equivalent surface area of 1 g of activated carbon made of coconut shell ranges from 1,100 to 1,400 m^2 [8]. Activated carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels [9]. In fixed-bed column operation, liquid solution is fed into the column from the top and it flows out from the bottom guided by gravity force in nature. During adsorption process, a zone known as mass transfer zone (MTZ) could be developed within the carbon bed, where adsorption occurs [10]. The MTZ can be considered as the region within the column in which the adsorbate changes from 10 to 90% of its inlet value [11]. An increase in effluent concentration can be observed when the MTZ reaches the outlet, where the solution exits the column.

1.1. Column adsorption theory

The bed depth service time (BDST) model is an equation derived from the surface reaction theory. The equation can be used to predict the breakthrough curve of the carbon bed [12, 13]. The equation is expressed as follows:

$$t = \left(\frac{N_a}{C_0 V} H\right) + \frac{1}{C_0 K} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (1)$$

where t is the time (min), C_t is the effluent concentration of the malathion (mg/L) and C_0 influent concentration of malathion (mg/L); K is the rate constant in BDST model (L/mg min); H, bed depth (cm); N_a, adsorption capacity (mg/L); t, service time (h); V, approach velocity (m/h).

A linear graph known as BDST graph can be obtained from the Adam–Bohart model by plotting a graph of service time (t) versus bed depth (H). At a particular breakthrough point, the BDST graph can be used to predict the various service times for the different bed depths. In addition, the constants that are needed to predict the breakthrough curves for the malathion adsorption can also be determined from the BDST graph. Eq. (1) can be rewritten in the form of a straight line [14].

$$t = aH - b \quad (2)$$

where a is slope of BDST line $a = \left(\frac{N_o}{C_0 V}\right)$ and the intercept of this equation represents as Eq. (3)

$$b = \frac{1}{C_0 K} \ln\left(\frac{C_0}{C_t} - 1\right) \quad (3)$$

Thus, N_o and K can be evaluated from slope (a) and the intercept (b) of the plot of t versus H, respectively.

The objectives of this study are to determine the efficiency of granular-activated carbon (GAC) made of coconut shell and palm shell in removing insecticide (i.e., malathion) from aqueous solution, and to evaluate the adsorption performance of the selected GAC through column test. These evaluations are important to assess the effectiveness of GAC as an alternative filter medium to remove pesticides from water environment or wastewater.

2. Materials and methods

2.1. Adsorbent and adsorbate

In this study, GAC made of coconut shell and palm shell was utilized as the adsorbents, and malathion solution was used as the adsorbate. The GAC was supplied by a local manufacturer of GAC (Kekwa Indah Sdn. Bhd., Nilai, Negeri Sembilan). The malathion solution is prepared using malathion with formulation of 95% active ingredient, supplied by Sigma Aldrich. Malathion solution of 7 μg/L was adopted throughout the experiments.

The GAC was crushed using a stainless steel blender and sieved to a size of 1,000 μm. The 1,000 μm GAC was then washed with 1 M of HCl and rinsed repeatedly with deionized water in order to remove residual oil and impurities [15]. Then, the GAC was heated in an oven at 110˚C for 24 h stored in a sealed bottle.

2.2. Column tests procedures

The column tests were performed using a laboratory glass column with an internal diameter of 1.3 cm and a height of 120 cm. The column was packed with coconut shell–activated carbon (CSAC) and oil palm shell–activated carbon (PSAC) at different bed depths. During the test, aqueous solution was continuously fed to the column at a specified time. The initial concentration of the malathion solution was collected and predetermined before the test. The effluents of were intermittently collected and determined spectrophotometrically on a Cary 50 UV Spectrophotometer at 230 nm λ_{max}.

3. Results and discussion

3.1. Characterization of the adsorbents

The adsorbent was characterized for its various physical and chemical properties in order to understand the mechanism involved during the adsorption process. The selected pesticide was determined spectrophotometrically on a Cary 50 UV Spectrophotometer at 230 nm λ_{max}. The surface area and the pore size distributions for the activated carbons were measured using a Micrometric ASAP 2010 surface area analyzer according to nitrogen adsorption–desorption method [7].

3.2. Effect of empty bed contact time on breakthrough curves of CSAC and PSAC

Design of column test for adsorption was started with laboratory testing. GAC of different particles size are packed in the column. The pesticide solution (i.e., malathion) was then fed under gravity into the column. The effluents from the column were sampled at different intervals. The experimental conditions are summarized in Table 1.

Table 2 shows the value of surface area, pore volume, and pore radius of both adsorbents used in this study; CSAC and PSAC. The further discussion was reported by Jusoh et al. [7] in the previous study. It was found that the adsorption of CSAC and PSAC is favored in acidic condition. Adsorbent pH may influence the removal efficiency and become important factor of adsorption performance [16]. Since CSAC has a lower pH, this indicates that CSAC may be more favorable as compared to PSAC. With respect to ash content, the practical limit allowed in the activated carbon varies within 2–5%. Ash contents of the activated carbon are the residue that remains, when the carbonaceous portion is burned off. This is the inorganic, inert, amorphous, and unusable part present in the activated carbon. The results show that CSAC is well below the acceptable limit of 5% (i.e., 3%), whereas PSAC shows a higher ash content of 9%. The same trend was also observed by Acharya et al. [9] which clearly state that the ash content in the range of 3–4.45% resembles good adsorbents. On top of that, CSAC has lower moisture content and this indicates better adsorption efficiency because less adsorption sites are filled with water. Therefore, this demonstrates that CSAC has better adsorbent performance than PSAC.

Table 1
Experimental parameters for malathion adsorption by GAC

Parameters	Values
Flow rate, m^3/h	0.00012
Approach velocity, $m^3/(h.m^2)$	1.44
Column diameter, m	0.013
Adsorbent particles size, mm	1.000
Temperature, ˚C	30

Table 2
Physicochemical characteristics of CSAC and PSAC

	CSAC	PSAC
Surface area (m^2/g)	850	788
Pore volume (cm^3/g)	281	261
Median pore radius (Å)	21.78	17.27
pH	4.92	5.41
Ash content (%)	3.05	9.00
Moisture content (%)	5.10	7.10

The data obtained from the column test were used to plot the breakthrough curves for malathion. The breakthrough curves are shown in Fig. 1(a) and (b).

Some of the adsorption sites were occupied over the treatment period, and this resulted in increased concentration in the effluent. The effluent concentration continued to rise and it leveled off at $t = 6$ h. When all the adsorption sites were occupied, the influent and the effluent of the column were expected to show the same concentration. This indicated the occurrence of breakthrough and the column should be replaced or regenerated at this point. The effect of the different empty bed contact time (EBCT) on the breakthrough curve at a constant flow rate presented in Fig. 1(a) and (b). The results showed that the shape and gradient of the breakthrough curve was slightly different with the variation of EBCT. The higher uptake of malathion was observed at the beginning of the fixed-bed column operation, but the concentration of malathion in the effluent increased rapidly after the breakthrough time. It was found that the upper bed depth achieved saturation earlier than lower bed depth. As can be seen in Fig. 1, the t increased with the increase in bed depth. These results suggest that the increase in the malathion uptake in a column of increased bed depth is due to the increase in contact time for malathion adsorption [17].

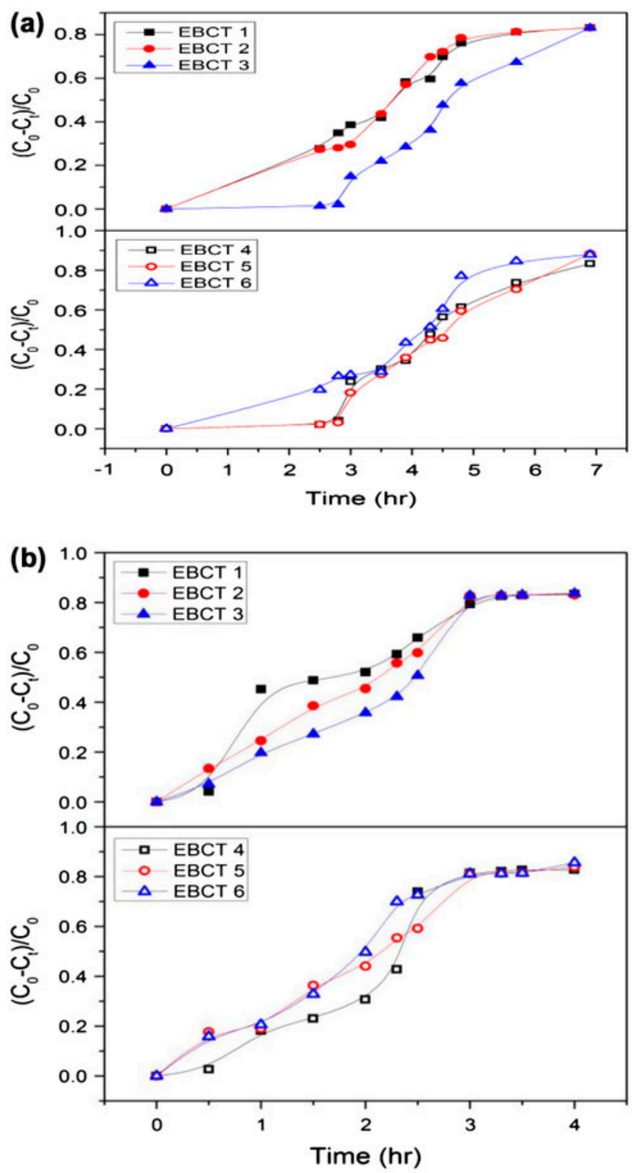

Fig. 1. Breakthrough curves for (a) coconut shell and (b) palm shell. EBCT 1 = 2.95 min; EBCT 2 = 3.93 min; EBCT 3 = 4.91 min; EBCT 4 = 11.76 min; EBCT 5 = 15.70 min; EBCT 6 = 19.60 min.

Fig. 1(a) and (b) represent the breakthrough at EBCT 1–6 for CSAC and PSAC, respectively. Similar trend was observed for the breakthrough curves produced by CSAC and PSAC. The results showed that higher uptake of malathion was observed at the beginning of the fixed-bed column, but the concentration of malathion in the effluent increased rapidly throughout the treatment period. Additionally, the breakthrough time increased with the increase in EBCT. The pesticide uptake capacities increased with the increase in EBCT. This is possibly due to increased surface area of the adsorb which provide more binding sites for the sorption. The results indicate that the increased in the malathion uptake with the increased in the EBCT in column is likely due to the longer contact time for malathion adsorption [15]. It can be seen from the Fig. 1(a) and (b) the adsorption efficiency was higher at longer EBCT. At higher EBCT, the residence time of the adsorbate was longer, so that the adsorbent got more time to bind with the pesticide efficiently. It was observed that the adsorbent achieved saturation easily at lower EBCT and the malathion uptake increased with increased in EBCT (Table 3). It is clear from Fig. 1(a) the exhaustion time for CSAC was slightly higher than PSAC due to the higher surface area of the CSAC 849 m^2/g compared with PSAC (788 m^2/g). This indicates that the column is able to remove the pesticides contaminant from the initial concentration of 7 μg/L to the effluent concentration of 1.20 μg/L.

3.3. Bed depth service time

The effect of bed depth on performance was studied using the BDST model. A plot of t versus bed depth (H) is shown in Fig. 2(a) and (b). The equations of linear relationship were obtained with the R^2 value of 0.98.

This indicates the validity of the BDST model for the present column system. The calculated adsorption

Table 3
Column data and parameters obtained at different EBCT and GAC

GAC	EBCT (min)	Percentage removal (%)
CSAC	2.95	28.6
	3.93	41.4
	4.91	50.0
	11.76	64.2
	15.7	71.4
	19.6	82.9
PSAC	2.95	18.6
	3.93	31.4
	4.91	42.9
	11.76	47.1
	15.7	60.0
	19.6	71.4

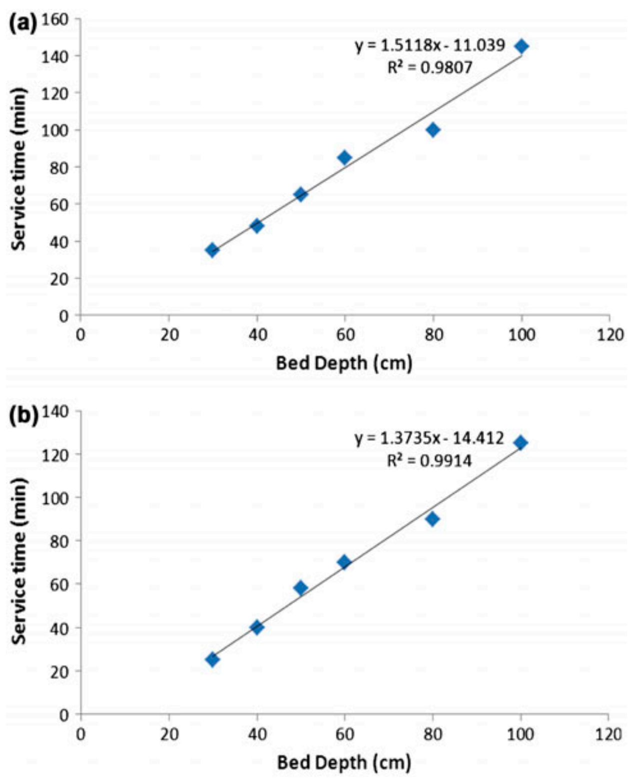

Fig. 2. BDST graph for (a) CSAC and (b) PSAC.

capacity (N_o) and the rate constant (K) are presented in Table 4. It was found that the adsorption capacity of CSAC was reduced from 0.086 to 0.056 mg/cm^3 at flow rates of 2 and 8 mL/min, respectively. A similar trend was observed for PSAC (Table 4). This illustrates that the adsorption capacity increased with decreased flow rate. The value of K and N_o indicated

Table 4
Calculated adsorptive capacity and rate constant for CSAC and PSAC

GAC	Q (ml/min)	No (mg/L)	K (L/mg/h)
CSAC	2	0.086	0.59
CSAC	8	0.056	1.05
PSAC	2	0.077	0.69
PSAC	8	0.031	1.58

that the CSAC is highly efficient for the removal of malathion from water environment. Table 4 shows the constant N_o and K for the CSAC and PSAC.

Fig. 2 indicates that the increase in bed depth could provide a longer service time. This agrees with Baral et al. [18] that reported the increased in carbon bed depth would increase the breakthrough time. The constant N_o and K obtained for CSAC and PSAC were substituted into Adam–Bohart equation, respectively. The result showed that higher EBCT gives better adsorption performance compared with the lower EBCT.

4. Conclusion

GAC was able to remove an initial concentration (7 μg/L) of malathion up to 83% (1.2 μg/L), showing encouraging performance in the adsorption of malathion. The experimental data were fitted well and was found to correlate the service time and bed depth of GAC in a linear correlation. The interpretation of Adam–Bohart model indicates that CSAC showed higher adsorption of malathion compared with that of PSAC. The extension of bed depth of GAC resulted in longer service time, and therefore, the time to reach breakthrough point could be extended.

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