REMOVAL OF ENDOSULFAN FROM WATER USING OIL PALM SHELL ACTIVATED CARBON AND RICE HUSK ASH

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ABSTRACT

In this study, the adsorption of endosulfan, a type of pesticide, onto agricultural waste-based adsorbents, namely, oil palm shell activated carbon (PSAC) and rice husk ash (RHA), was investigated. The as-received adsorbents were used for batch α- and β-endosulfan adsorption studies which included kinetics and equilibrium aspects at a constant solution pH of 5 and at a temperature of 25°C. It was found that removal of β-endosulfan by both adsorbents was significantly more efficient than that of α-endosulfan indicating a high affinity of PSAC and RHA towards β-endosulfan. Interestingly, kinetic equilibrium for β-endosulfan adsorption onto PSAC was achieved after 30 min of contact time with a very high capacity of 418 mg g⁻¹. The adsorption kinetics data fitted the pseudo-second order model well, implying chemisorption was the rate-controlling step. Equilibrium adsorption data for PSAC fit the Freundlich isotherm better than the Langmuir isotherm, suggesting the existence of multi-layer adsorption of endosulfan on a relatively heterogeneous PSAC surface. It was found that PSAC was efficient in removing β-endosulfan from water while it was conversely true for RHA.

INTRODUCTION

The agro-pesticide industry is one of the most important supporting industries in the agricultural sector in Malaysia. Modern agriculture is reliant on the utilization of agrochemicals such as pesticides, and, in recent years, the agrochemical industry has shown tremendous growth as these pesticides are increasingly being used in almost all agricultural fields in the country. The total number of active ingredients registered with the Pesticide Board of Malaysia, as of 1990, was 189 (Anon., 1990). Concurrently, there are also great environmental concerns associated with the use of pesticides such as endosulfan, which was widely used in the Malaysian agricultural industry in the early 1990s. The most significant adverse effect of pesticides is contamination of hydrological systems. Surface waters are vulnerable to contamination by pesticides as most agricultural and urban areas drain pesticides into the waterways. Subsequently, they can be transported downstream and dispersed into rivers, lakes, reservoirs and the ocean.

Endosulfan is a chlorinated hydrocarbon insecticide which acts on contact as a poison for a wide range of insects. Technically, endosulfan consists of two isomers, α- and β-endosulfan, in the ratio of 70:30. Both of these isomers have dissimilar physical properties such as melting point, aqueous solubility and vapour pressure. It is widely believed that endosulfan is an endocrine disruptor, and can also adversely affect human development. Endosulfan has been detected at levels ranging from 1 to 313 ng litre⁻¹ in numerous rivers in Peninsular Malaysia. Concentrations of endosulfan in sediment samples from Bernam River, Malaysia, were found to be 960 ng litre⁻¹ (Vijayaletchumy, 1992).

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Recent methods studied for the removal of endosulfan from the water environment include ozone oxidation (Yazgan and Kinaci, 2003), ponded wetland (Rose *et al.*, 2006) and biological treatment (Kumar and Philip, 2006a). Adsorption of endosulfan using suitable adsorbents is also one of the common methods for removing it from streams. Previous studies pertaining to this method include adsorption using wood charcoal (Sudhakar and Dikshit, 1999), soil (Ismail *et al.*, 2002; Kumar and Philip, 2006b) and metal nanoparticles (Sreekumaran-Nair *et al.*, 2003). Cost of the adsorbent material is a significant factor for its industrial application in removing contaminants from wastewater streams. As such, there is much research currently being conducted in developing low-cost adsorbents derived from industrial and agriculture wastes.

Malaysia is one of the world's top producers of palm oil, and this industry produces large quantities of solid wastes, among which is palm shell. Palm shell activated carbon (PSAC) is produced by subjecting the palm shell to thermal activation (physical activation) followed by chemical activation using suitable chemicals (Guo and Lua, 2000). On the other hand, rice husk, a by-product of the rice milling industry, accounts for about 20% of the whole rice grain (Daifullah *et al.*, 2003). Rice husk heaps are present in abundance in rice mills throughout Malaysia. Rice husk ash (RHA) is a resultant material from combustion of rice husk. Rice husk currently presents a disposal dilemma in Malaysia due to its abundance. It should be noted that adsorption of endosulfan using PSAC and RHA has not been investigated previously, and that results presented herewith represent information which is beneficial to researchers seeking alternative technologies to remove pesticides from water. As such, the objective of the study was to investigate adsorption of α- and β-endosulfan onto PSAC and RHA. Adsorption rate and equilibrium data were fitted to kinetic models, namely, pseudo-first and pseudo-second order as well as established isotherm models (the Freundlich and the Langmuir). The effects of contact time and adsorbent dosage on the adsorption of endosulfan were also studied.

MATERIALS AND METHODS

Materials

Endosulfan (99.8% purity) was obtained from Sigma-Aldrich in solid form. A synthetic solution was made by accurately weighing 5 mg of endosulfan and dissolving it into one litre of hexane. The solution was mixed using a magnetic stirrer until the compound was completely dissolved.

PSAC was obtained from Kekwa Indah Sdn Bhd in Nilai, Negeri Sembilan. It was ground and sieved to produce particles of sizes ranging from 53 mm to 1.18 mm. The ground PSAC was then washed thoroughly with distilled water to remove impurities and unwanted moisture. Subsequently, the PSAC was dried in an oven at 103°C for 24 hr, cooled at room temperature, and finally stored in a desiccator. The physical properties of PSAC are shown in *Table 1*.

TABLE 1. PHYSICAL PROPERTIES OF PALM SHELL ACTIVATED CARBON (PSAC)*

Property/parameter	Value
Maximum pore volume	0.358723 cm^3 g^{-1}
Median pore diameter	6.2759 x 10^{-10} m
Surface area per volume of pores	1.66 x 10^9 m^2 m^{-3}
Surface area	595.3149 m^2 g^{-1}
Specific gravity of PSAC	0.5135

Source: *Leong (1998).

Rice husk was obtained from BERNAS Rice Mill, Kuala Selangor. Rice husk was burnt for 24 hr in a ferrocement furnace. After combustion, the resultant ash was left to cool inside the furnace overnight before being taken out. The ash was then ground using a Los Angeles machine which consisted of a grinding chamber with an opening at the top. The chamber was set to rotate for 5000 revolutions using an electrical motor at a speed of 33.3 rpm. The resultant RHA was blue-grey in colour and appeared to be very fine. Elements found in RHA were determined using dispersive X-ray (EDX) spectroscopy (EDAX DX-4), and they are listed in *Table 2*. The surface area of RHA was determined to be approximately 10 m^2 g^{-1} by a Micromeritics ASAP 2010 adsorption apparatus. All chemicals used were reagent grade.

Adsorption Studies

Batch adsorption studies were carried out by agitating 1 g of either PSAC or RHA with 100 ml aqueous solution of 5 mg $litre^{-1}$ of endosulfan in a

TABLE 2. ELEMENTS OF RICE HUSK ASH

Element	% weight
Carbon (C)	28.80
Oxygen (O)	50.93
Silica (Si)	3.59
Iron (Fe)	8.97
Aluminum (Al)	2.12
Nickel (Ni)	5.59

temperature-controlled shaker at 150 rpm. The solution pH was adjusted to 5 whereas the temperature of the solution was maintained at 25°C. Samples were withdrawn at certain time intervals and filtered through 0.45 μm membrane filter for kinetics determination. For the isotherm studies, flasks containing different dosages of either PSAC or RHA were agitated for 24 hr, after which the resultant solutions were filtered for endosulfan analysis. The adsorption capacity was calculated using the equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \qquad (1)$$

where q_t (mg g^{-1}) is the adsorption capacity at time t, C_0 and C_t (mg litre^{-1}) are the concentrations of endosulfan in solution initially and at time, t, V (L) is the volume and M (g) is the weight of activated carbon (AC). The concentration of endosulfan in solution was determined using a gas chromatography – mass spectrometer (GC-MS).

RESULTS AND DISCUSSION

Effect of Contact Time

The data on the adsorption of α- and β-endosulfan by PSAC and RHA with respect to contact time are shown in *Figure 1*. Interestingly, the removal of β-endosulfan by both adsorbents was significantly more efficient th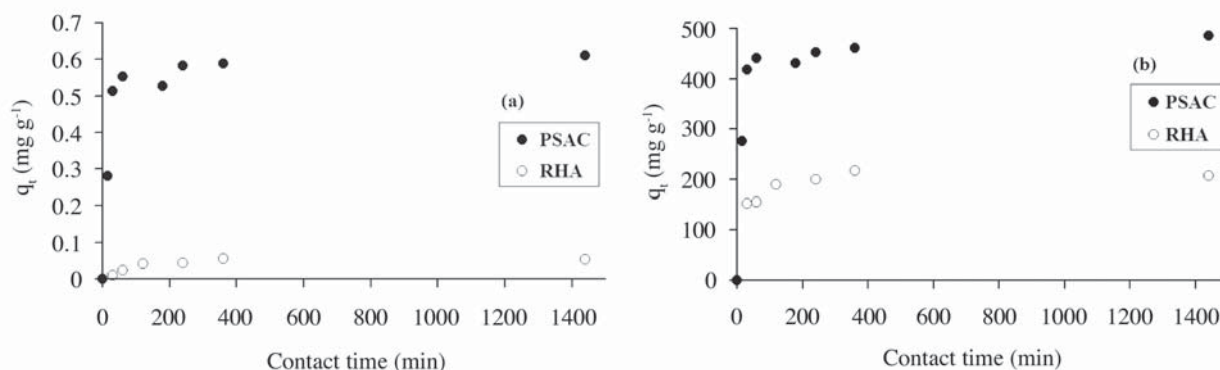an that of α-endosulfan. This implies that both PSAC and RHA are, perhaps, more selective towards β-endosulfan. For α-endosulfan adsorption by PSAC, equilibrium was reached after 30 min of contact time whereas for RHA equilibrium was reached after 2 hr of contact time. The maximum adsorption capacities in terms of kinetic equilibrium for PSAC and RHA were determined to be 0.51 mg g^{-1} and 0.04 mg g^{-1}, respectively. Kinetic equilibrium for β-endosulfan adsorption onto PSAC was achieved after 30 min of contact time with an adsorption capacity of 418 mg g^{-1}. The equilibrium for β-endosulfan adsorption by RHA was achieved after 2 hr of contact time with a capacity of 190 mg g^{-1}. The substantially shorter equilibrium time for adsorption using PSAC was expected as the surface area of PSAC is significantly higher than RHA enabling a faster adsorption rate for PSAC.

The adsorption rate constants of α- and β-endosulfan onto PSAC and RHA were determined by using the pseudo-second order model (Erhan *et al.*, 2004):

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (2)$$

The plot of t/q_t against t produces a linear relationship from which k_2, the rate constant of the pseudo-second order adsorption (g mg^{-1} min^{-1}), and q_e, the adsorption capacity at equilibrium (mg g^{-1}), are determined from the slope and intercept of the plot, respectively.

Table 3 shows the parameters of adsorption kinetics of the pseudo-second order model. It was observed that the adsorption kinetics data fitted the

Figure 1. Kinetics of (a) α- and (b) β-endosulfan adsorption onto palm shell activated carbon (PSAC) and rice husk ash (RHA).

TABLE 3. PARAMETERS OF ADSORPTION KINETICS OF THE PSEUDO-SECOND ORDER MODEL

	PSAC			RHA		
	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
α-endosulfan	0.11	0.62	1.00	0.057	0.057	0.99
β-endosulfan	1.37 x 10^{-4}	500.00	1.00	5.09 x 10^{-4}	208.00	1.00

Notes: PSAC - palm shell activated carbon.
     RHA - rice husk ash.

pseudo-second order model very well ($R^2 > 0.98$). It should be noted that the adsorption kinetics data were also fitted to the pseudo-first order model but its R^2 value was less than 0.8 indicating poor fit. Therefore, the pseudo-first order model was omitted from further discussion for reasons of brevity. These results suggest that the endosulfan adsorption system adhered to the pseudo-second order kinetics which further suggests that chemisorption is the rate-controlling step (Namasivayam and Prathapa, 2007). From *Table 3*, it is obvious that the rate of adsorption of α-endosulfan was significantly higher than of β-endosulfan. This result is in agreement with the result of a kinetics study conducted by Kumar and Philip (2006a) in which adsorption of α-endosulfan onto Indian soil was higher than β-endosulfan. They further explained that the arrangement/position of ions in the crystal lattice/stereoisomerism might be responsible for the variation in the rate of adsorption. *Table 4* shows the comparison of adsorption capacities of endosulfan on different adsorbents.

Effect of Adsorbent Dosage

The effects of PSAC and RHA dosages on the percentage removal of α- and β-endosulfan are depicted in *Figure 2*. The percentage of endosulfan sorption increased with PSAC and RHA dosages. For α-endosulfan adsorption onto PSAC, the removal efficiency was from 47% to 91% whereas adsorption by RHA indicated percentage removal ranging from 3 to 18%. For β-endosulfan, removal efficiencies for PSAC were between 64% and 95% whereas for RHA the values were between 4% and 17%. *Figure 3* shows the effects of PSAC and RHA dosages on adsorption capacities of α- and β-endosulfan. The results show that the adsorption capacities for α- and β-endosulfan decreased with an increase in PSAC dosage from 0.25 g to 2.0 g while adsorption capacities for both types of endosulfan onto RHA were relatively constant. The maximum adsorption capacities for RHA were observed to be 0.13 mg g^{-1} for α-endosulfan and 70 mg g^{-1} for β-endosulfan. Results obtained further indicate that the adsorption sites on RHA were perhaps saturated at a dosage of 1 g whereas it appeared that an increase in PSAC dosage provided more free (or unused) adsorption sites on its surface.

Adsorption Isotherms

The equilibrium data on the adsorption of endosulfan onto PSAC and RHA were fitted to two

TABLE 4. COMPARISON OF ADSORPTION CAPACITIES OF ENDOSULFAN ON DIFFERENT ADSORBENTS

Adsorbent	q, α-endosulfan (mg g^{-1})	q, β-endosulfan (mg g^{-1})	pH	Reference
Indian composted soil	0.3876[a]	0.2018[a]	7.37[b]	Kumar and Philip (2006a)
Indian clayey soil	0.4480[a]	0.2722[a]	8.46[b]	Kumar and Philip (2006a)
Indian sandy soil	0.1083[a]	0.0942[a]	8.48[b]	Kumar and Philip (2006a)
Red soil	0.2186[a]	0.1966[a]	7.20[b]	Kumar and Philip (2006a)
Palm shell activated carbon	0.62	500	5	Present study
Rice husk ash	0.057	208	5	Present study

Notes: [a] Denotes maximum adsorption capacity.
[b] pH of adsorbent (immersed in distilled water with endosulfan).
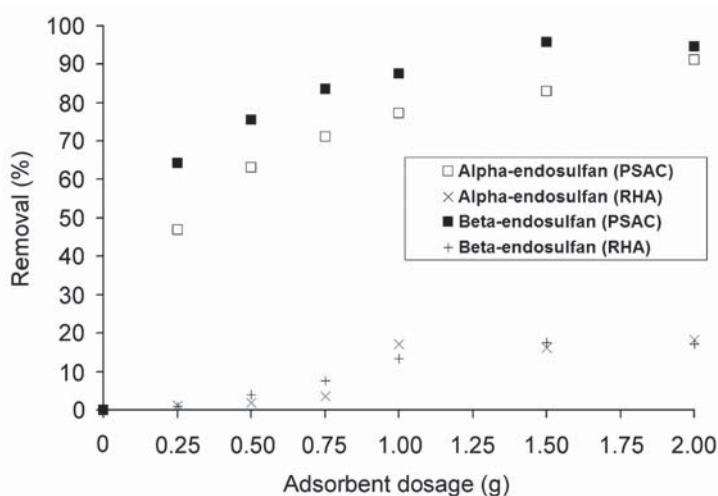

Figure 2. Effects of palm shell activated carbon (PSAC) and rice husk ash (RHA) dosages on the percentage removal of α- and β-endosulfan.
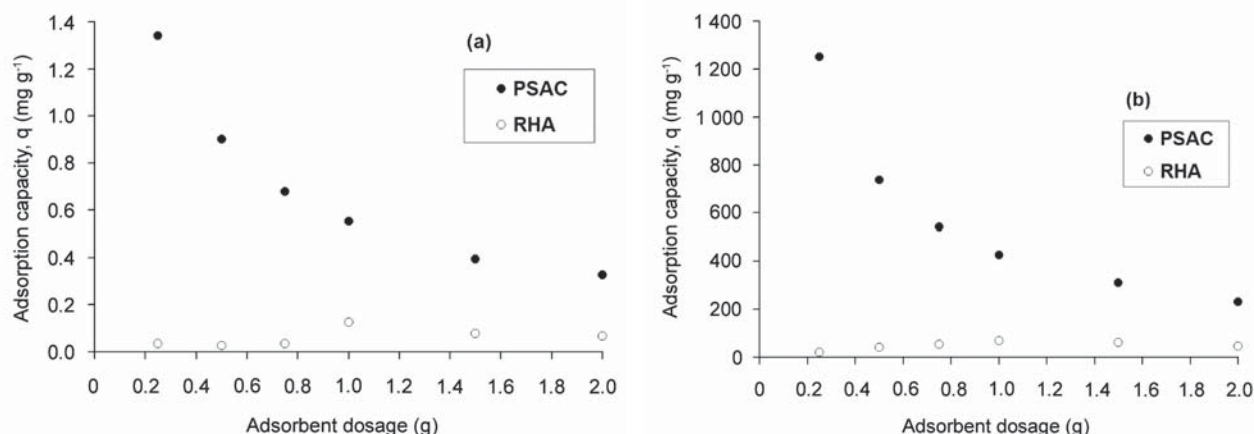
Figure 3. Effects of palm shell activated carbon (PSAC) and rice husk ash (RHA) dosages on the adsorption capacities (contact time = 24 hr) of (a) α- and (b) β-endosulfan.

isotherm models, namely, the Langmuir and the Freundlich. The Langmuir isotherm model, which is a two-parameter model, is based on monolayer adsorption on active sites of the adsorbent, and is presented in Equation (3):

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{3}$$

where q_m is the amount of adsorbate adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage, and K is the Langmuir constant. Use of this adsorption isotherm implies that intermolecular forces diminished quickly with distance, and also the existence of a monolayer of adsorbate at the outer surface of the adsorbent. A linear plot of (C_e/q_e) against C_e was employed to give values of q_m and K from the slope and the intercept of the plot, respectively (Monser and Adhoum, 2002). Another two parameter isotherm model, namely, the Freundlich isotherm model, is represented by Equation (4):

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F and n are constants. The Freundlich isotherm is obtained assuming a very heterogeneous surface. A linear plot of log q_e against log C_e is employed to provide values of K_F and n from the

intercept and slope of the plot, respectively (Chingombe *et al.*, 2006).

The determined Langmuir and Freundlich isotherm constants for adsorption of endosulfan onto PSAC and RHA at 25°C along with their correlations of determination are listed in *Table 5*. It is apparent that the adsorption data for PSAC fitted the Freundlich isotherm better than the Langmuir isotherm because the R^2 values for the former were comparatively higher than the latter suggesting the existence of multilayer adsorption of endosulfan on a relatively heterogeneous PSAC surface. Interestingly, adsorption data for RHA showed a contrasting result in that they fitted the Langmuir isotherm better. Nonetheless, the negative K and n values of adsorption of both α- and β-endosulfan onto RHA implies that RHA was not favourable for the removal of endosulfan from water. It is the opinion of the authors that this was probably attributed to the low surface area of RHA ($\approx$10 m² g⁻¹) which inhibited adsorption.

CONCLUSION

Generally, the removal of β-endosulfan by both adsorbents was significantly more efficient than removing α-endosulfan, indicating high affinity of PSAC and RHA towards β-endosulfan. The kinetics data clearly fitted the pseudo-second order model

TABLE 5. EQUILIBRIUM ISOTHERM CONSTANTS FOR ADSORPTION OF ENDOSULFAN ONTO PALM SHELL ACTIVATED CARBON (PSAC) AND RICE HUSK ASH (RHA) AT 25°C

		Langmuir constants			Freundlich constants		
		q_m (mg/g)	K	R^2	K_F	n	R^2
α-endosulfan	PSAC	5.89	0.069	0.19	0.4	1.24	0.94
	RHA	7.61×10^{-3}	-0.18	0.90	2.42×10^3	-0.18	0.82
β-endosulfan	PSAC	2 500	4.08×10^{-4}	0.42	6.21	1.46	0.89
	RHA	7.31	-2.56×10^{-4}	0.59	5.48×10^{15}	-0.26	0.50

very well, implying that chemisorption was the rate-controlling step in this study. Adsorption sites on RHA were perhaps saturated at a dosage of 1 g while it appeared that an increase in PSAC dosage provided more free (or unused) adsorption sites on its surface. Adsorption data for PSAC fitted the Freundlich isotherm better than the Langmuir isotherm, suggesting the existence of multilayer adsorption of endosulfan on a relatively heterogeneous PSAC surface. RHA was not favourable for the removal of endosulfan from water because the K and n values of adsorption for both α- and β-endosulfan onto RHA were found to be negative.

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