CHAPTER 6

CONTINUOUS ADSORPTION

In order to obtain, the experiment of batch parameters can provide essential information of the process about the effectiveness of the adsorption processes. Nevertheless for the operation of industrial scale continuous adsorption system, fixed-bed column procedures are an absolute. Therefore, the fixed-bed column of chitosan (CH), blended chitosan/PVA 1:1 (CH/PVA), benzoyl chitosan (BCH), quateraminated chitosan (QCH), chitosan-sodium lauryl sulfate (CH-SDS), chitosan-hexadecyltrimethy ammonium bromide (CH-C-Tab), chitosan- polyoxyethylene sorbitanmonooleate (CH-Tween 80), blended chitosan/PVA-sodium lauryl sulfate (BCH-SDS), blended chitosan/PVA-hexadecyltrimethy ammonium bromide (BCH-C-Tab) and blended chitosan/PVA-polyoxyethylene sorbitanmonooleate (BCH-Tween 80) were investigated in this thesis using basic adsorption column design parameters. Furthermore, chitosan, blended chitosan/PVA 1:1 and chitosan-sodium lauryl sulfate (CH-SDS) studies were bring to evaluate the effects of bed depth and the inlet flow rate of adsorption of cutting fluids. In addition, the analysis of the breakthrough curve was done by using a model of bed depth/ service time (BDST). Double two columns were employed also in this studies. The detail of all presented in the following section:

6.1. Single column

Initially, cutting fluids was adsorbed by the adsorbent resulting in residual in the effluent. Adsorption occurred continuously and the adsorbate concentration in the effluent gradually rose. In the upflow mode, when cutting fluids was introduced at the bottom of a clean bed of the adsorbents, most of cutting fluids removal initially occurred in a narrow band at the bottom of the column. This step was called the adsorption zone. As column operation continues, the lower layers of the adsorbent became saturated with cutting fluids and the adsorption zone progressed upward through the bed. Eventually, the adsorption zone reached the top of the column and the cutting fluids concentration in the effluent began to increase. A breakthrough curve of column was obtained by plotting the adsorbate concentration in the effluent against time. The breakthrough curves for cutting fluids with initial concentration 1.00 % w/v, pH 3 flow rate 0.5 cm^3/min and bed depth 20 cm, of chitosan, blended chitosan/PVA 1:1, CH-C-Tab, CH-Tween 80, BCH-C-Tab and BCH-Tween 80 as adsorbents are shown in Figure 6.1. The point on the breakthrough curve at which the cutting fluids concentration reaches its maximum permissible value (100 mg/l) is referred to as a breakthrough. The breakthrough times (corresponding to C/C_0 = 0.10) are 8 min for chitosan, 12 min for blended chitosan/PVA 1:1, and 5 min for CH-C-Tab, CH-Tween 80, BCH-C-Tab and BCH-Tween 80. The point where the effluent cutting fluids concentration reaches 90 % of the influent cutting fluids is called the point of column exhaustion. Then, the exhaustion times, C/C_0 = 0.9, were 90 min for chitosan, 163 min for blended chitosan/PVA 1:1, 63 min for CH-C-Tab, 30 min for CH-Tween 80 and BCH-C-Tab, 55 min for BCH-Tween 80. The volume of cutting fluids treated at the breakthrough point were 4.0 cm^3 for chitosan, 6.0 cm^3 for blended chitosan/PVA 1:1, CH-C-Tab, CH-Tween 80, BCH-C-Tab and BCH-Tween 80 as adsorbents. At the exhaustion point were 45.0 cm^3 for chitosan, 81.5 cm^3 for blended chitosan/PVA 1:1, 31.5 cm^3 for CH-C-Tab, 15.0 cm^3 for CH-Tween 80 and BCH-C-Tab and 27.5 cm^3 for BCH-Tween 80. All results are summarized in Table 6.1.

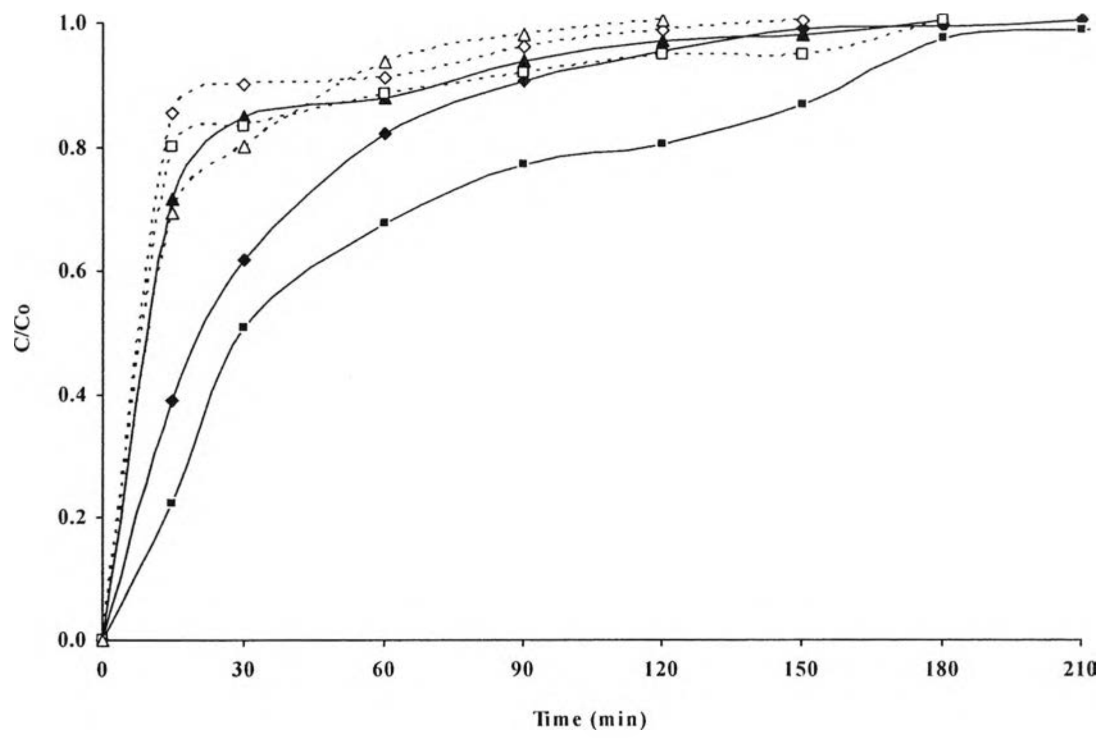

Figure 6.1 Breakthrough profiles for cutting fluids adsorption on ♦ chitosan, ■ blended chitosan/PVA 1:1, ▲ CH-C-Tab, ◊ CH-Tween 80, □ BCH-C-Tab and △ BCH-Tween 80

Table 6.1 Experimental results of single column studies on chitosan, blended chitosan/PVA 1:1, CH-C-Tab, CH-Tween 80, BCH-C-Tab and BCH-Tween 80

Adsorbents	Breakthrough time (min)	Exhaustion time (min)	Volume of treated cutting fluids (cm^3)	
			Breakthrough point	Exhaustion point
Chitosan	8	90	4.0	45.0
Blended chitosan/PVA 1:1	12	163	6.0	81.5
CH-C-Tab	5	63	2.5	31.5
CH-Tween 80	5	30	2.5	15.0
BCH-C-Tab	5	63	2.5	31.5
BCH-Tween 80	5	55	2.5	27.5

The breakthrough curves for cutting fluids, initial concentration 1.00 % w/v, pH 3 flow rate 0.5 cm^3/min and bed depth 20 cm, of benzoyl chitosan, quateraminated chitosan, CH-SDS and BCH-SDS as adsorbents are shown in Figure 6.2. The breakthrough times were 0.7 and 4.5 h for benzoyl chitosan and quateraminated chitosan, respectively. The breakthrough time of CH-SDS and BCH-SDS were obtained at 0.3 h. The point where the effluent of cutting fluids concentration reaches 90 % of the influent of cutting fluids were 80 h for benzoyl chitosan, 154 h for quateraminated chitosan, 80 h for CH-SDS and 100 h. for BCH-SDS, respectively. The volume of cutting fluids treated at the breakthrough point was 21 cm^3 for benzoyl chitosan, 135 cm^3 for quateraminated chitosan, 9 cm^3 for CH-SDS and BCH-SDS, respectively. The exhaustion point was 2400 cm^3 for benzoyl chitosan, 4620 cm^3 for quateraminated chitosan, 2400 cm^3 for CH-SDS and 3000 cm^3 for BCH-SDS, respectively. Table 6.2 summarized the result obtained from this study.

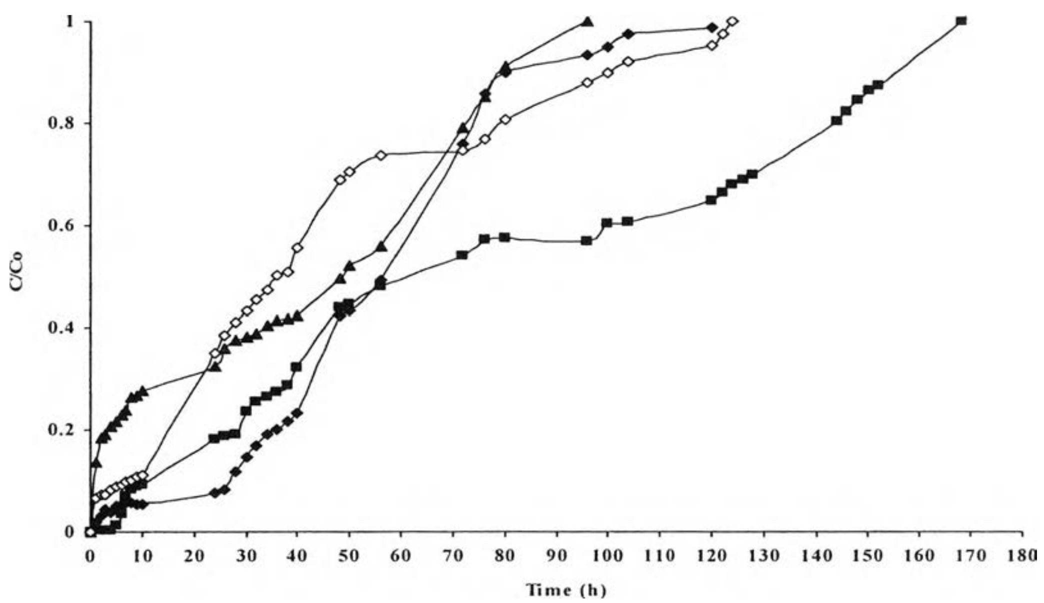

Figure 6.2 Breakthrough profiles for cutting fluids adsorption on ♦ benzoyl chitosan, ■ quateraminated chitosan, ▲ CH-SDS and ◊ BCH-SDS

Table 6.2 Experimental results of single column studies on benzoyl chitosan, quateraminated chitosan, CH-SDS and BCH-SDS

Adsorbents	Breakthrough time (h)	Exhaustion time (h)	Volume of treated cutting fluids (cm^3)	
			Breakthrough point	Exhaustion point
Benzoyl chitosan	0.7	80	21	240
Quateraminated chitosan	4.5	154	135	4620
CH-SDS	0.3	80	9	2400
BCH-SDS	0.3	100	9	3000

6.2. Evaluation of basic design parameter for continuous adsorption

Formation and movement of an adsorption zone can be evaluated mathematically [12, 61, 62]. The time required for the adsorption zone to move up the length of its own height up the column once it has established is

$$t_z = \frac{V_s}{Q_w} \tag{6.1}$$

where t_z is the time required for the adsorption zone (min), V_s is the total volume of cutting fluids spiked water treated between breakthrough and exhaustion (l) and Q_w is the influent flow rate (cm^3/min).

The time required for establishing the adsorption zone and move completely out of the bed is

$$t_E = \frac{V_E}{Q_w} \tag{6.2}$$

where t_E is the time required for establishing the adsorption zone and move completely out of the bed (min) and V_E is the total volume of cutting fluids treated to the point of exhaustion (l).

The rate at which the adsorption zone is moving up or down through the bed is

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \tag{6.3}$$

where U_z is the rate of the adsorption zone (cm/min), h_z is the height of the adsorption zone (cm), h is the height of bed depth (cm) and t_f is the time required for the adsorption zone to initially form (min).

Rearranging Equation 6.3 provides an expression for the height of the adsorption zone.

$$h_z = \frac{h t_z}{t_E - t_f} \tag{6.4}$$

The value of t_f cannot be measured directly but the limits for t_f can be established by further analysis of the adsorption zone. At breakthrough point, the fraction of adsorbate present in the adsorption zone still haring processing ability to remove adsorbate was

$$F = \frac{S_z}{S_{\max}} = \frac{\int_{V_B}^{V_E} (C_0 - C_t)\,dV}{C_0 (V_E - V_B)} \tag{6.5}$$

where F is the breakthrough fraction, C_0 is the initial cutting fluids concentration (mg/l), C_t is the cutting fluids concentration at time t, V_B is the total volume of cutting fluids to the point of breakthrough (l), S_z is amount of cutting fluids that has been removed by the adsorption zone from breakthrough to exhaustion and S_{max} is the amount of cutting fluids removed by the adsorption zone if completely exhausted.

If the adsorption zone is saturated at breakthrough, the value of F will be very close to zero and the time required for the zone to initially form (t_f) will be approximately the same as the time required for the zone to move up a distance equal to its own height. If the adsorption zone is practically free of adsorbate at the breakpoint, i.e., $F \approx 0$, the time required for zone formation is very short. If the concentration front is characterized by a typical S-shaped curve, F is approximately 0.5. Thus, time for required the adsorption zone to initially form

$$t_f = (1 - F)t_z \tag{6.6}$$

The percentage of the total column saturation at breakthrough is

$$\%\,Saturation = \frac{h + (F - 1)h_z}{h} \times 100 \tag{6.7}$$

Comparing the results in Table 6.3 and 6.4, it is found that chitosan, blended chitosan/PVA 1:1, CH-C-Tab, BCH-C-Tab, CH-Tween 80 and BCH-Tween 80 spent time for adsorption zone shorter than benzoyl chitosan, quateraminated chitosan, CH-SDS and BCH-SDS. It this noticed that, the height of the adsorption zone shown in Table 6.3 and 6.4 are in the same ordering narrow in a range varies from 28.6 to 39.9 cm. For the rate of the adsorption zone, it is found that chitosan, blended chitosan/PVA 1:1, CH-C-Tab, BCH-C-Tab, CH-Tween 80 and BCH-Tween 80 (Table 6.3) show the rate of the adsorption zone higher than benzoyl chitosan, quateraminated chitosan, CH-SDS and BCH-SDS. Percentage of saturation at breakthrough of chitosan, blended chitosan/PVA 1:1, CH-C-Tab, BCH-C-Tab, CH-Tween 80 and BCH+Tween 80 in Table 6.3 obtained are lower than benzoyl chitosan, quateraminated chitosan, CH-SDS and BCH-SDS in Table 6.4. It can be concluded that hight column may not suitable for the adsorption of cutting fluids due to low percentage of breakthrough.

Table 6.3 Basic parameters for fixed bed of cutting fluids onto chitosan, blended chitosan/PVA 1:1, CH-C-Tab, BCH-C-Tab, CH-Tween 80 and BCH-Tween 80

Adsorbents	t_z (min)	h_z (cm)	U_z (cm/min)	% Bed saturation
Chitosan	82	33.5	0.408	16.33
Blended chitosan/PVA 1:1	198	35.7	0.180	10.81
CH-C-Tab	58	34.1	0.588	14.71
BCH-C-Tab	58	34.1	0.588	14.71
CH-Tween 80	25	28.6	1.143	28.57
BCH-Tween 80	75	35.3	0.471	11.76

Table 6.4 Basic parameters for fixed bed of cutting fluids onto benzoyl chitosan, quateraminated chitosan, CH-SDS and BCH-SDS

Adsorbents	t_z (min)	h_z (cm)	U_z (cm/min)	% Bed saturation
Benzoyl chitosan	4758	39.3	0.008	1.73
Quateraminated chitosan	8970	37.7	0.004	5.68
CH-SDS	4782	39.7	0.008	0.75
BCH-SDS	5982	39.8	0.007	0.60

6.3. Effect of flow rate

To investigate the effect of flow rate on cutting fluids adsorption, the initial concentration cutting fluids was held constant at 1.00 % w/v and pH was kept at pH 3 while flow rate was varied 0.50, 1.00 and 2.00 cm^3/min, respectively. The breakthrough curves are shown in Figure 6.3 for chitosan, Figure 6.4 for blended chitosan/PVA 1:1 and Figure 6.5 for CH-SDS, respectively.

It can be seen that breakthrough time generally is shorter when increasing in flow rate. The exhausted time for chitosan, blended chitosan/PVA 1:1 and CH-SDS was 90 min, 210 min and 80 h, respectively when flow rate was 0.5 cm^3/min. When, increasing flow to 1.0 cm^3/min exhausted time was shorter to 30 min for chitosan, 95 min for blended chitosan/PVA 1:1 and 24 h for CH-SDS. Further increase flow rate to 2.0 cm^3/min, exhausted time was to 13 min for chitosan, 90 min for blended chitosan/PVA 1:1 and 8 h for CH-SDS, respectively. A lower flow rate of cutting fluids influent, attached time between cutting fluids and adsorbents is long. Therefore, more cutting fluids can be removed from the effluent. The variation in the slope of breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. At higher flow rate, the rate of mass transfer increases. It introduced that the amount of cutting fluids adsorbed on unit bed height increases with flow rate. Then longer time to reach saturation is show when lower flow rate is employed [63].

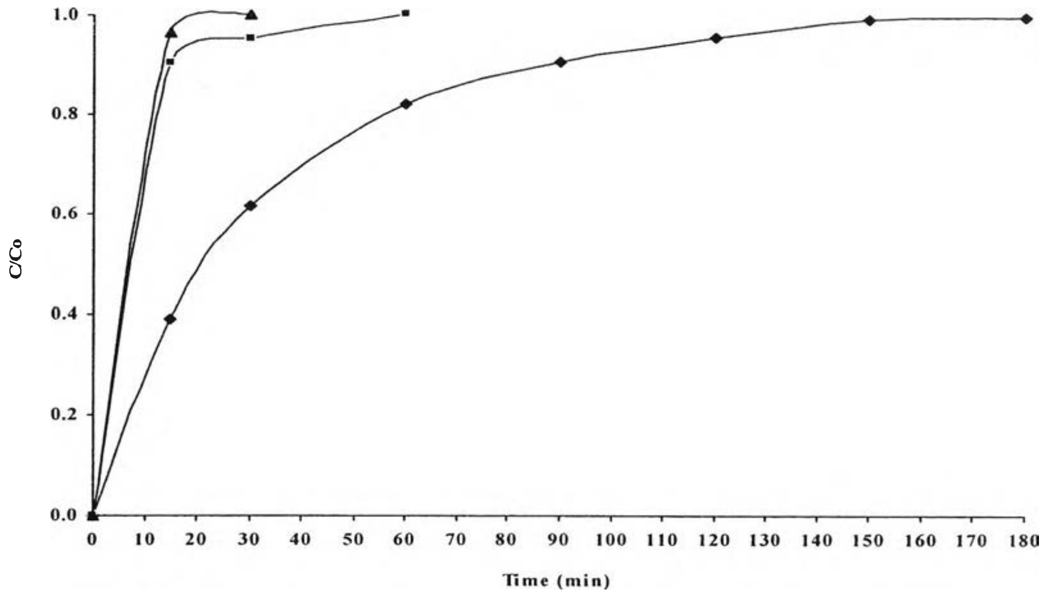

Figure 6.3 Breakthrough curves adsorption cutting fluids of chitosan at flow rate ♦ 0.50, ■ 1.00 and ▲ 2.00 cm^3/min

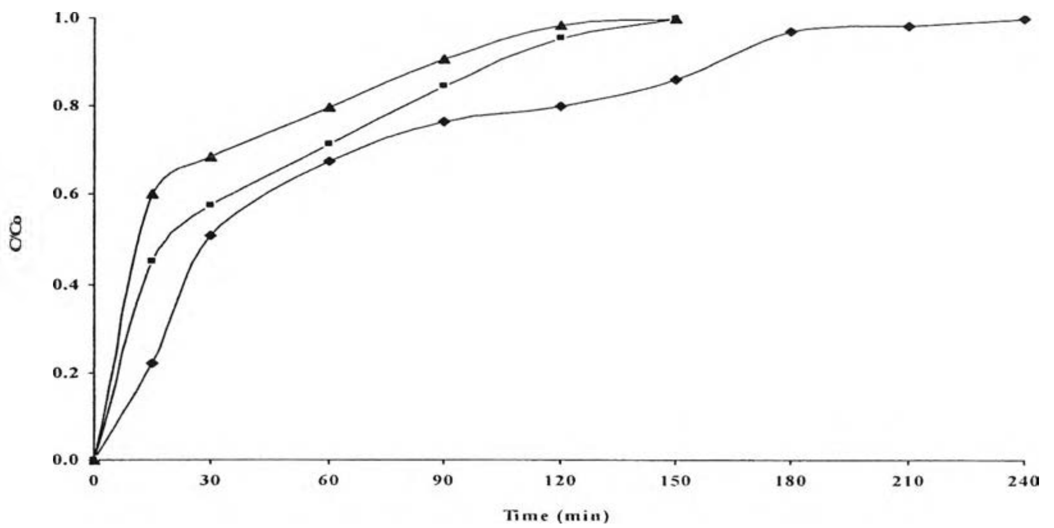

Figure 6.4 Breakthrough curves adsorption cutting fluids of blended chitosan/PVA 1:1 at flow rate ♦ 0.50, ■ 1.00 and ▲ 2.00 cm^3/min

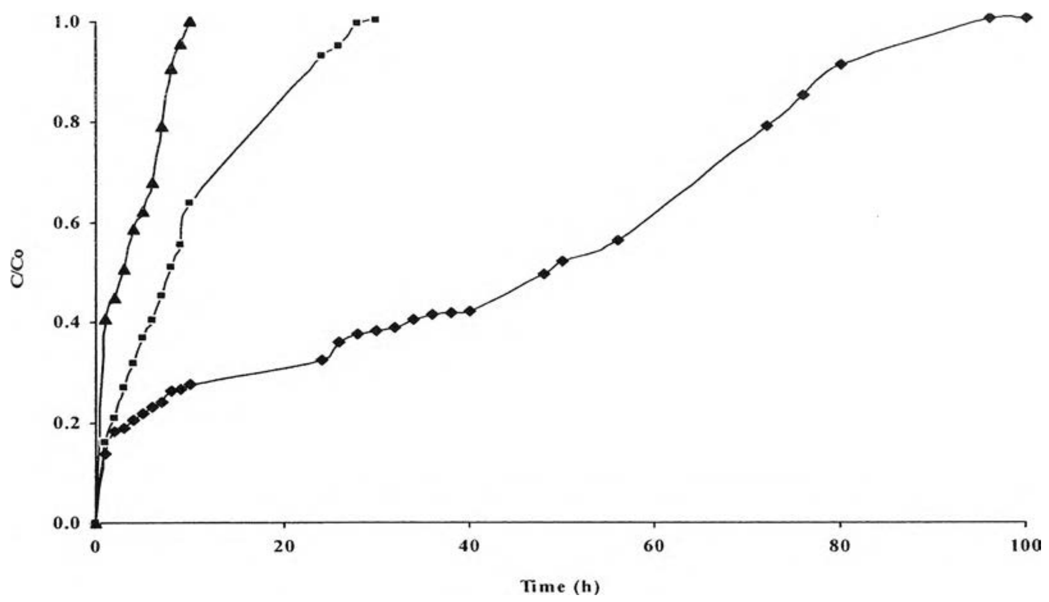

Figure 6.5 Breakthrough curves adsorption cutting fluids of CH-SDS at flow rate ♦ 0.50, ■ 1.00 and ▲ 2.00 cm^3/min

6.4. Effect of bed height

Figures 6.6 to Figure 6.8 show effect of bed height on adsorption of cutting fluids on chitosan, blended chitosan/PVA 1:1 and CH-SDS when using 1.0 % w/v initial cutting fluids concentration at pH 3 at flow rate 0.5 cm^3/min. The bed depth was varied from 5 to 20 cm. More cutting fluids are adsorbed when increasing in bed height. This can be explained that cutting fluids more time to contact with adsorbents. This results in higher remove efficiency of cutting fluids. The exhausted time for chitosan, blended chitosan/PVA 1:1 and CH-SDS was 90 min, 210 min and 80 h at bed depth 20 cm. When the bed depth was 15 cm, the exhausted time was 65 min for chitosan, 88 min for blended chitosan/PVA 1:1 and 55 h for CH-SDS. When still reducing the bed height to 10 cm, it was found that the exhausted time was 60 min for chitosan, 35 min for blended chitosan/PVA 1:1 and 38 h for CH-SDS. When reducing the height to 5 cm, the exhausted time changed to 35 min for chitosan, 38 min for blended chitosan/PVA 1:1 and 32 h for CH-SDS. The higher bed column results in a decrease in the cutting fluids concentration in the effluent. The slope of the breakthrough curve decreased with increasing bed height. Higher uptake is obtained at higher bed height due to an increase in the surface area of adsorbents, which provides more binding sites for the adsorption [64, 65].

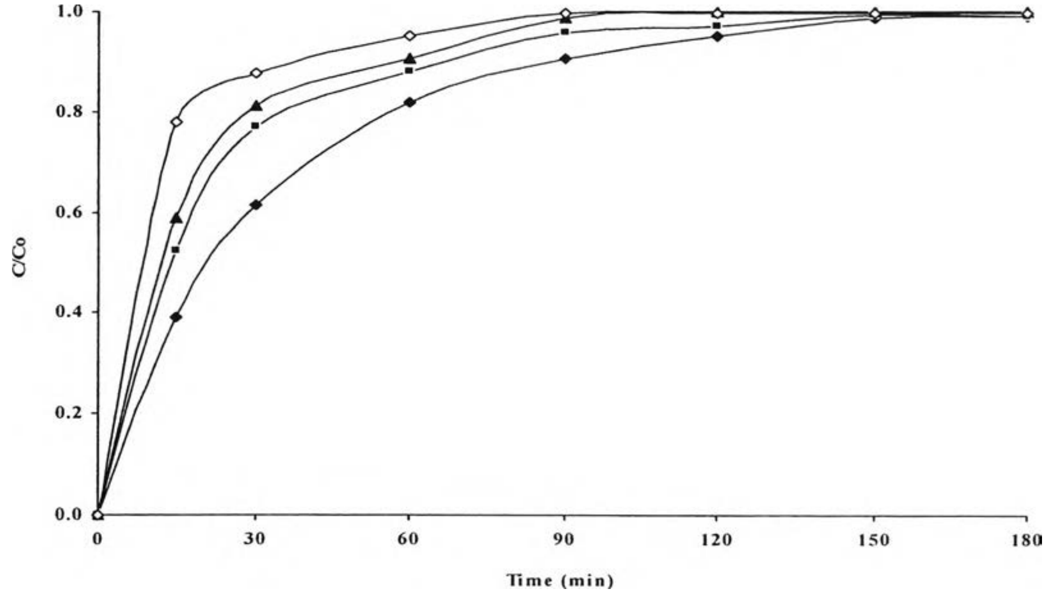

Figure 6.6 Breakthrough curves adsorption cutting fluids of chitosan at bed depth

♦ 20.0, ■ 15.0, ▲ 10.0 and ◊ 5.0 cm

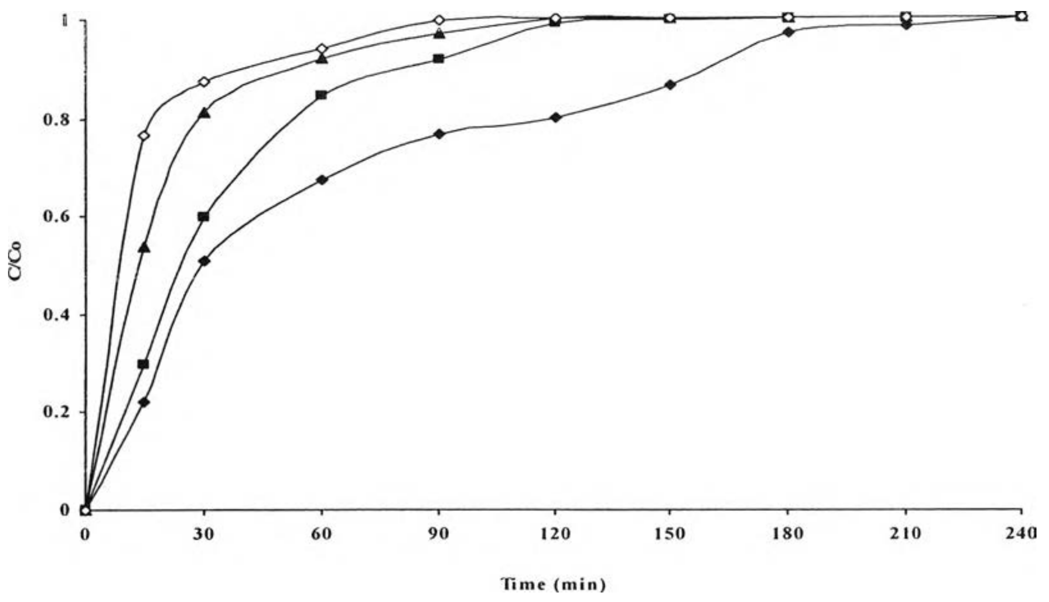

Figure 6.7 Breakthrough curves adsorption cutting fluids of blended chitosan/PVA 1:1at bed depth ♦ 20.0, ■ 15.0, ▲ 10.0 and ◊ 5.0 cm

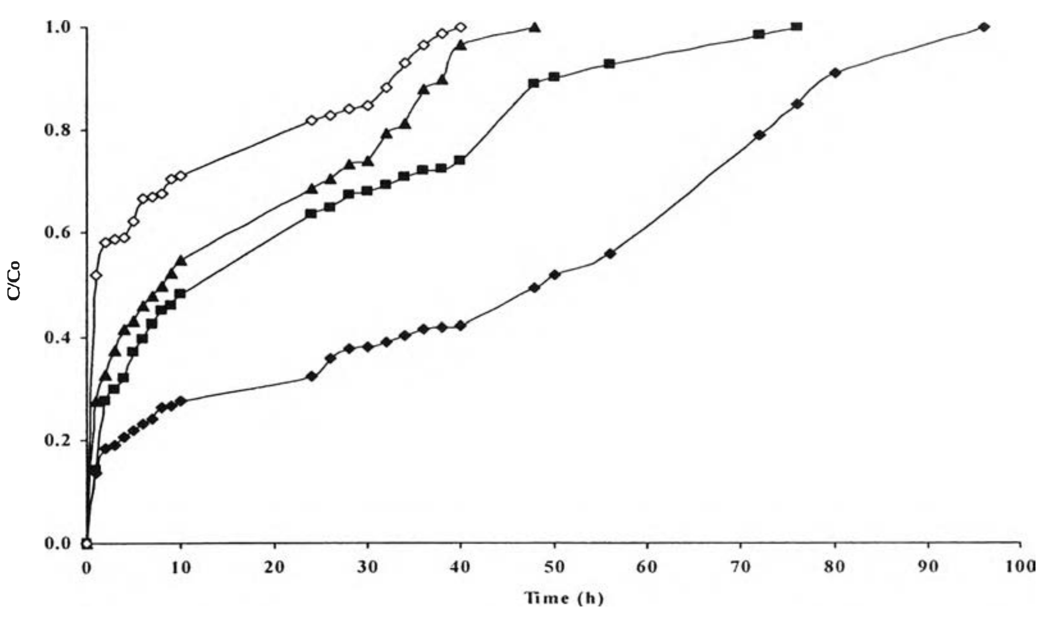

Figure 6.8 Breakthrough curves adsorption cutting fluids of CH-SDS at bed depth ♦ 20.0, ■ 15.0, ▲ 10.0 and ◊ 5.0 cm

6.5. Analysis column data based on bed depth/service time model

The bed depth/service time (BDST) model was extended to predict and determine breakthrough time and exhaustion time at different flow rates. The BDST model is based on physically measuring the capacity of the bed at different breakthrough values. The BDST model works well and provides useful modeling equations for the changes of system parameters. A modified form of the equation that expresses the service time at breakthrough, t, as a fixed function of operation parameter is the BDST model [62, 66-69]:

$$t = \frac{N_0}{C_0 v} Z - \frac{1}{C_0 K_a} \ln\left(\frac{C_0}{C_t} - 1\right) \qquad (6.8)$$

where t is the time (min), Z is the bed depth of column (cm), C_0 is the initial concentration of cutting fluids in the liquid phase (mg/L), v is the influent linear velocity (cm/min), N_0 is the adsorption capacity (mg/l), K_a is the rate constant in the BDST model (l/mg-min) and C_t is the effluent concentration of cutting fluids in the liquid phase (mg/l).

A plot of t versus Z should yield a straight line where N_0 and K_a, the adsorption capacity and rate constant, can be evaluated.

$$t = aZ + b \qquad (6.9)$$

where

$$a = \frac{N_0}{C_0 v} \qquad (6.10)$$

$$b = \frac{1}{K_a N_0} \ln\left(\frac{C_0}{C_t} - 1\right) \qquad (6.11)$$

The slope constant for a different flow rate can be directly calculated by

$$a' = a\frac{v}{v'} = a\frac{Q}{Q'} \qquad (6.12)$$

where a and v are the old slope and influent linear velocity, respectively and a' and v' are the new slope and influent linear velocity. As the column used in experimental has the same diameter, the ratio of original (v) and new influent linear velocity (v') and original flow rate (Q) and the new flow rate (Q').

For other influent concentrations, the desired equation is given by a new slope and a new intercept is given by

$$a' = a\frac{C_0}{C_0'} \tag{6.13}$$

$$b' = b\frac{C_0}{C_0'}\frac{\ln(C_0' - 1)}{\ln(C_0 - 1)} \tag{6.14}$$

where b' is the new and old intercept, respectively, C'_0 and C_0 is the new and old influent concentration, respectively.

The lines of t and Z at values of C_t/C_0 0.2, 0.4 and 0.6 when employing chitosan, blended chitosan/PVA 1:1 and CH-SDS are shown in Figure 6.9, 6.10 and 6.11, respectively. The related constants of BDST according the slopes and intercepts of line are summarized in Table 6.5. When increasing in C_t/C_0 increased, the rate constant K_a decreases while the adsorption capacity of the bed per unit bed volume, N_0, increases. From the values of correlation coefficient, the validity of the BDST model is suitable for the present system. The BDST model constants can help to scale up the process of continuous adsorption for the other flow rate without further experimental runs [68]. The BDST equation obtained at a flow rate of 0.5 cm^3/min was used to predict the adsorbent performance at a higher flow rate of 1.0 cm^3/min. The predicted time (t_c) and experimental time (t_e) are shown in Table 6.6. A good prediction has been made for the case of changed flow rate.

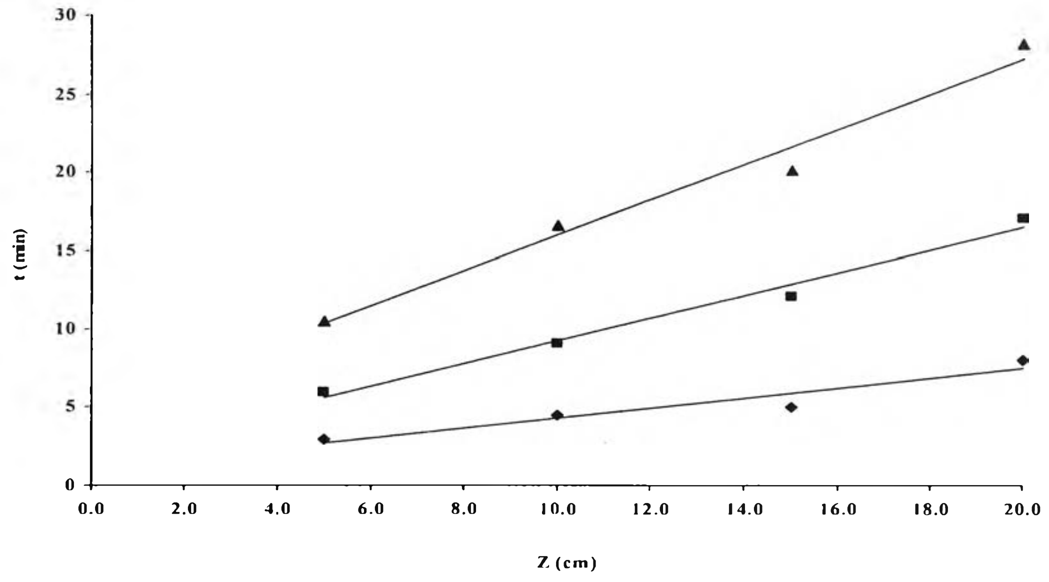

Figure 6.9 Isoremoval lines for different bed depth heights on chitosan

♦ C_t/C_0 = 0.2, ■ C_t/C_0 = 0.4 and ▲ C_t/C_0 = 0.6

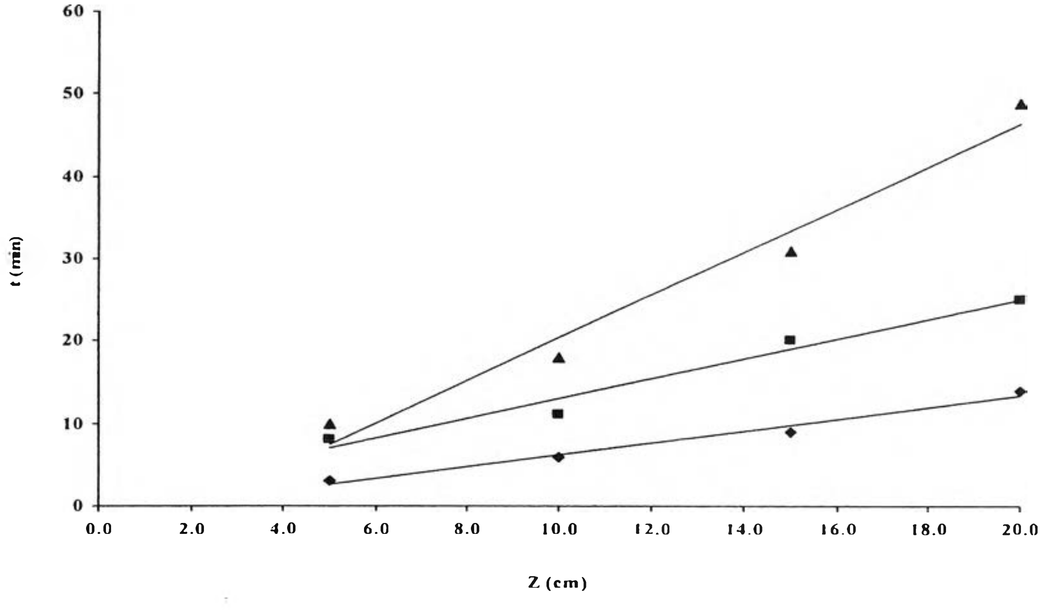

Figure 6.10 Isoremoval lines for different bed depth heights on blended chitosan/PVA 1:1 ♦ C_t/C_0 = 0.2, ■ C_t/C_0 = 0.4 and ▲ C_t/C_0 = 0.6

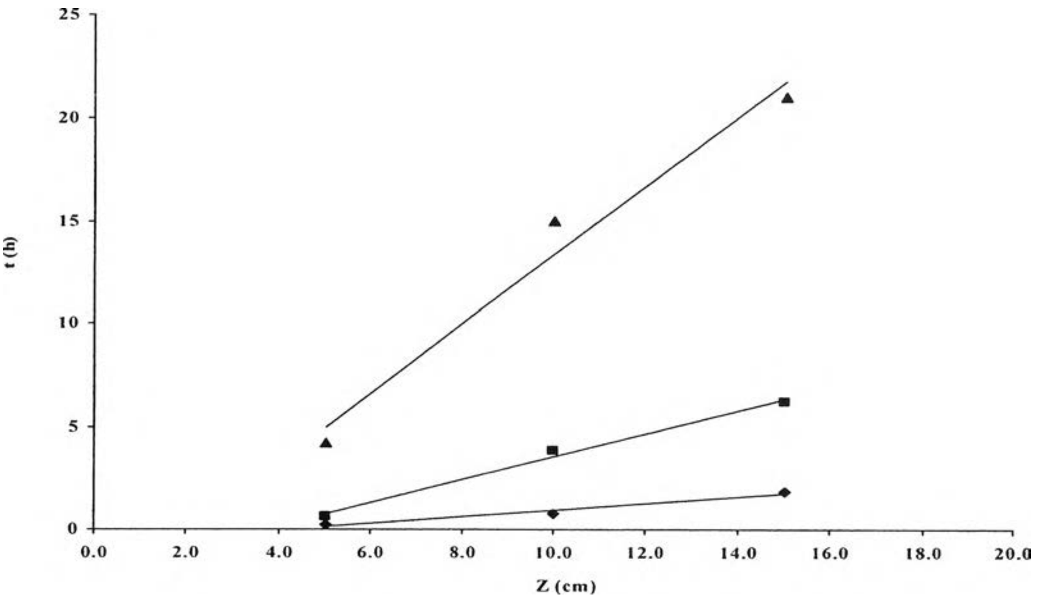

Figure 6.11 Isoremoval lines for different bed depth heights on CH-SDS

♦ C_t/C_0 = 0.2, ■ C_t/C_0 = 0.4 and ▲ C_t/C_0 = 0.6

Table 6.5 Calculated constants of BDST model for the cutting fluids on chitosan

C_t/C_0	a (min/cm)	b (min)	K_a (l/mg/min)	N_0 (mg/l)	R^2
0.2	0.31	1.25	7.00×10^{-5}	491.32	0.919
0.4	0.72	2.00	4.37×10^{-5}	1141.13	0.982
0.6	1.12	4.75	1.84×10^{-5}	1775.09	0.979

Table 6.6 Predicted breakthrough time based on BDST constant for a new flow rate on chitosan

C_t/C_o	a (min/cm)	b (min)	v (cm/min)	v' (cm/min)	a' (min/cm)	Z (cm)	t_c (min)	t_e (min)
0.2	0.31	1.25	0.10	0.20	0.16	20.0	1.9	3.5
0.4	0.72	2.00	0.10	0.20	0.36	20.0	5.2	4.9
0.6	1.12	4.75	0.10	0.20	0.56	20.0	6.5	8.8

Table 6.7 Calculated constants of BDST model for the cutting fluids on blended chitosan/PVA 1:1

C_t/C_0	a (min/cm)	b (min)	K_a (l/mg/min)	N_0 (mg/l)	R^2
0.2	0.72	-1.00	$-8.75x10^{-5}$	1141.13	0.971
0.4	1.20	1.00	$8.75x10^{-5}$	1901.88	0.968
0.6	2.60	-5.50	$-1.59x10^{-5}$	4120.74	0.982

Table 6.8 Predicted breakthrough time base on BDST constant for a new flow rate on blended chitosan/PVA 1:1

C_t/C_o	a (min/cm)	b (min)	v (cm/min)	v' (cm/min)	a' (min/cm)	Z (cm)	t_c (min)	t_e (min)
0.2	0.72	-1.00	0.10	0.20	0.36	20.0	8.2	14
0.4	1.20	1.00	0.10	0.20	0.60	20.0	11.0	25
0.6	2.60	-5.50	0.10	0.20	1.30	20.0	31.5	51

Table 6.9 Calculated constants of BDST model for the cutting fluids on CH-SDS

C_t/C_0	a (min/cm)	b (min)	K_a (l/mg/min)	N_0 (mg/l)	R^2
0.2	0.16	-0.67	-1.31E-04	253.58	0.951
0.4	0.56	-2.07	-4.22E-05	887.54	0.993
0.6	1.68	-3.40	-2.57E-05	2662.63	0.974

Table 6.10 Predicted breakthrough time based on BDST constant for a new flow rate on CH-SDS

C_t/C_o	a (min/cm)	b (min)	v (cm/min)	v' (cm/min)	a' (min/cm)	Z (cm)	t_c (h)	t_e (h)
0.2	0.16	-0.67	0.10	0.20	0.11	20.0	2.8	3.5
0.4	0.56	-2.07	0.10	0.20	1.03	20.0	7.7	34.0
0.6	1.68	-3.40	0.10	0.20	2.30	20.0	20.2	79.0

The predicted time obtained from chitosan blended chitosan/PVA 1:1 and CH-SDS is close to the experimental value. It was foud that the BDST model and constants evaluated can be used to design a column over a range of feasible flow rate at C_t/C_0 0.2, 0.4 and 0.6, respectively. These results also indicate the equation which is used to predict adsorption performance when operation at other condition.

6.6. Two columns

The breakthrough curves for a two column, initial cutting fluids concentration 1.00 % w/v, pH 3 flow rate 0.5 cm^3/min and bed depth 10 cm of chitosan as adsorbents are shown in Figure 6.12. The breakthrough times were 6 and 1 minutes for circular glass columns A and B, respectively. The point where the effluent cutting fluids concentration reaches 90 % of the influent cutting fluids was 100 and 55 minutes, respectively. The volume of cutting fluids spiked water treated at the breakthrough point was 3.0 and 0.5 cm^3 for the double two column, respectively and at the exhaustion point was 50 and 27.5 cm^3, respectively.

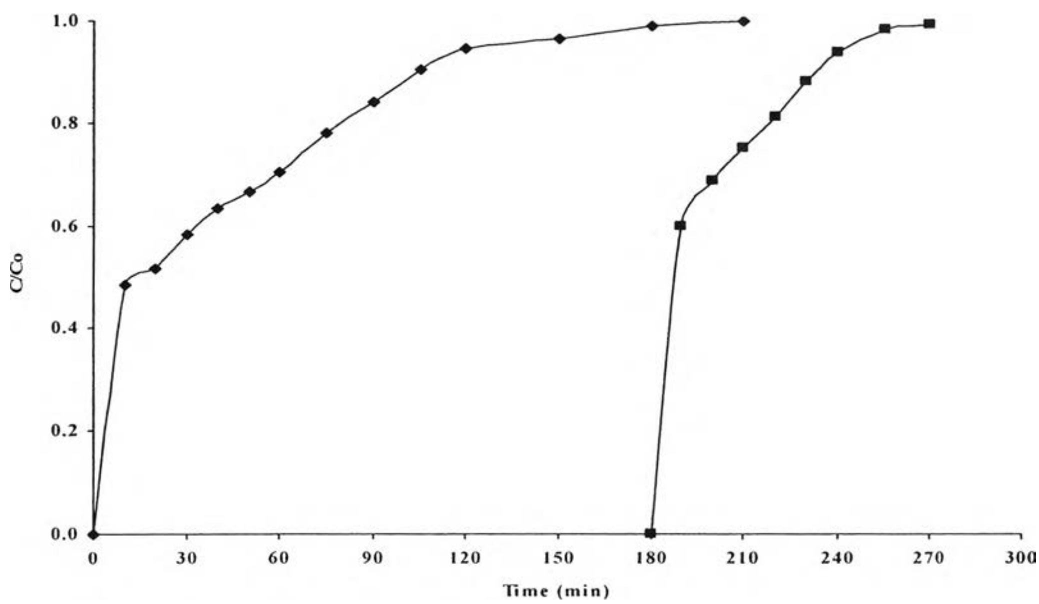

Figure 6.12 Breakthrough curve of adsorption of cutting fluid on chitosan type two column ♦ column A and ■ column B

The breakthrough curves for a two column, initial cutting fluids concentration 1.00 % w/v, pH 3 flow 0.5 cm^3/min and bed depth 10 cm of CH-SDS as adsorbents are shown in Figure 6.13. The breakthrough times were 0.3 and 0.1 h for circular glass columns A and B, respectively. The point where the cutting fluids effluent concentration reaches 90 % of the influent cutting fluid was 29 and 47 h, respectively.

The volume of cutting fluids spiked water treated at the breakthrough point was 9 and 3 cm^3 for the two column, respectively and at the exhausting point was 870 and 1410 cm^3, respectively.

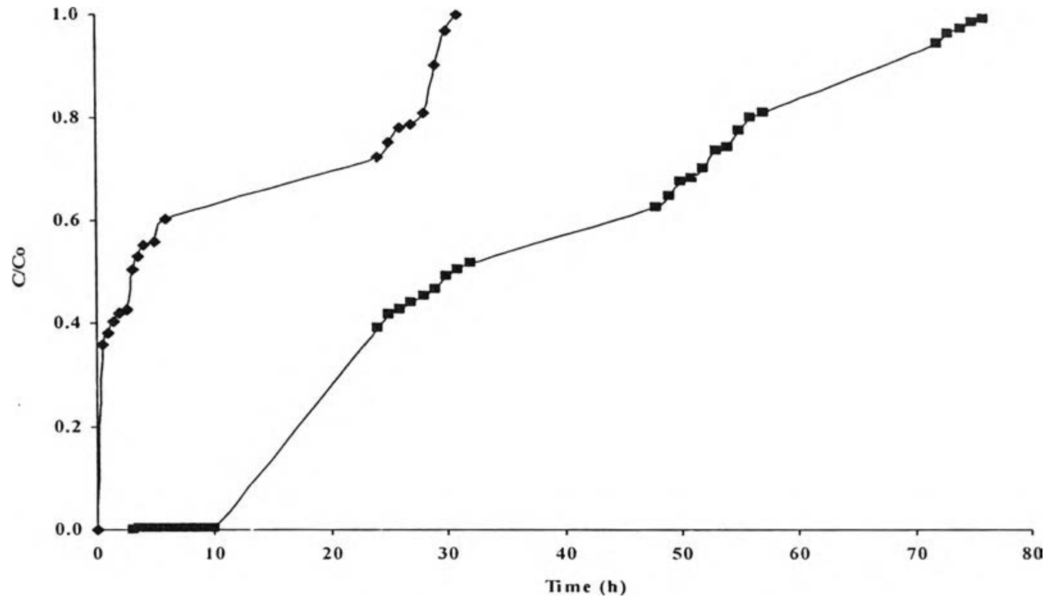

Figure 6.13 Breakthrough curve of adsorption of cutting fluids on CH-SDS type two column ♦ column A and ■ column B

Table 6.11 Basic parameters of two columns on chitosan and CH-SDS

Adsorbents	Type of column	t_z (min)	h_z (cm)	U_z (cm/min)	% Bed saturation
Chitosan	Two columns (A)	94.0	17.7	0.189	11.32
	Two columns (B)	54.0	19.3	0.357	3.57
CH-SDS	Two columns (A)	1722.0	19.6	0.011	2.05
	Two columns (B)	2814.0	19.9	0.007	0.42