Modification of Synthetic Zeolite Pellets from Lignite Fly Ash B : Treatability Study

Chaiwat Rongsayamanont[1], Khajornsak Sopajaree[2]

[1]Chiang Mai University, Department of Environmental Engineering, Muang, Chiang Mai, Thailand; [2]Associated Professor, Chiang Mai University, Department of Environmental Engineering, Muang, Chiang Mai, Thailand

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ABSTRACT

The present study examined the use of modified synthetic zeolite pellet (zeolite Na-P1), which were presented and discussed earlier in the previous paper, for the removal of cadmium from aqueous solution.The effects of pH, contact time and initial concentration on the sorption process were examined.The optimum pH was found to be 4.0.For batch study, residual cadmium concentration reached equilibrium in 1500 min and the removal efficiency were more than 98% in all formula of modified zeolite pellet and initial concentration. Langmuir model was fitted to explain the equilibrium of this sorption successfully which the maximum capacity of 3.14 mg/g. while are much lower than other low-cost adsorbents. For column study series application was investigated for the hydraulic loading rate (HLR) at 3.75 and 5.63 $m^3/(m^2$-hr) using initial cadmium concentration 6.6 mg/l. of synthetic wastewater. The adsorption capacity of 0.26 and 0.19 mg/g.,respectively were obtained by Bohart - Adams model. This showed that the lower HLR or upper bed depth would have higher breakthrough volume due to an increase in empty bed contact time (EBCT) and optimum EBCT in column should not be less than 3.39 min.

1. Introduction

As previous study, the synthetic zeolites in the form of pellet have been developed and modified.Therefore, the objective of this treatability study is to use modified zeolites pellet to remove cadmium ion from the wastewater and find its optimum conditions both batch and column study.

2. Material and Method

2.1. Material

The synthetic zeolite pellets in this study were developed and modified followed the method that mentioned earlier in the previous study. With differentiation in the amount of pore forming agents, there were 5 formulas of synthetic zeolites (See table 1) and all of them were used in this present study. The wastewater used in this

study was prepared by dilution of cadmium ion (II) sulfate solution (3CdSO4 8H2O) (Fluka AR grade) into deionized water to the concentration of of 6-100 mg/l. Sulfuric acid and NaOH were used for pH adjustment.

2.2. Batch study

The effect of pH on removal efficiency was carried out by shaking 1 ± 0.10 g of modified zeolite pellets(each formula) with cadmium ion solution of 6 mg/l (30 ml) at room temperature. The pHs of the mixtures were then adjusted to pH 2-8. After that, the mixtures were then shaken in the shaker operated at 200 rpm. After 35 hrs of being shaken, the solution was separated by vacuum filtration. The cadmium ion concentration in the supernatant was then measured by using Atomic Absorption Spectrophotometer, AAS. The efficiency of cadmium removal at all pHs then were calculated and the pH value at the maximum of cadmium removal was selected to be used in the next experiment.

The effects of contact time and initial concentration on adsorptive capacity were carried out by shaking 1 ± 0.10 g of modified zeolite pellets (each formula) with cadmium ion solution of 6-100 mg/l (30 ml) at room temperature. The pHs of the mixtures were then adjusted to the value that received from the last experiment. After that, the mixtures were then shaken in the shaker operated at 200 rpm. The contact times were selected appropiately between 0 - 35 hrs. When each contact time was reached, the mixture was withdrawn from the shaker, and the solution was seperated by vacuum filtration. The cadmium concentration in the supernatant was then measured by AAS. Then, the adsorption capacity for each formula were calculated.

2.3. Column study

In this study the selected modified zeolite pellet formula were crushed and filled into four acrylic columns that were connected in series. Each column had the inside diameter of 1.9 cm and the bed depth of each column was 10.6 cm. The synthetic wastewater had cadmium ion concentration of 6.6 mg/l and was fed into the column with the hydraulic loading rate of 3.75 and 5.63 m^3/m^2-hr at room temperature. Samples of each column effluent were periodically collected.

Table 1. Characteristics of modified zeolite pellet used in this study

Modified Zeolite Pellet	BET $(m^2./g.)$	App. Densiity (g/cm^3)	Hardness (Kg.)	% Abrasion (%)	CEC (meq/g.)
0P	8.37	2.40	8	0.2	0.28
5P	11.88	2.48	9	0.2	0.25
10P	10.45	2.41	9	0.2	0.35
15P	28.68	2.46	10	0.1	0.55

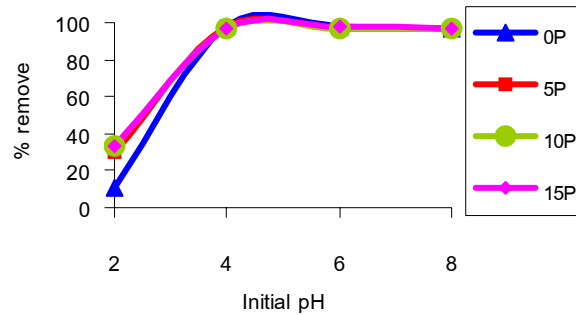## 3. Results and discussion

3.1. Effect of pH

Fig.1 Effect of initial pH in removal of 6 mg/LCd which each formula of modified zeolite pellet
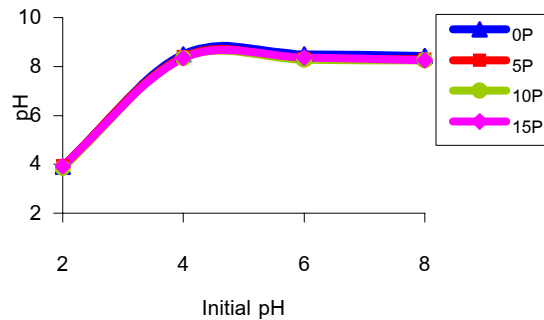

Fig.2 Effect of initial pH to pH after removal of 6 mg/LCd which each formula of modified zeolite pellet

Fig.1 and 2 showed the changes of pHs and cadmium removal efficiencies at various initial pHs after 35 hours of agitation, it clearly showed that the pHs of the mixture were sharply changed when lower initial pHs (initial pH of 2-4) were applied. However, at the higher initial pH values, the pHs of the mixture were quite constant. These Phenomena probably was resulted from two causes. The first cause may be due to the solid surface performs itself as the Lewis base as shown in the equation (1) and (2) [1]

$$Al - OH + H^+ \rightarrow Al - OH_2^+ \qquad (1)$$
$$Si - OH + H^+ \rightarrow Si - OH_2^+ \qquad (2)$$
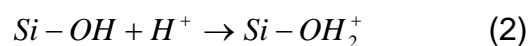
Al-OH and Si-OH represent solid surface phase, and they trend to be positive charges when H^+ concentrations in the solution are high (lower pH). This circumstance is coincided with the lower cadmium ion removal efficiency at lower pH (see Fig.2) which is resulted from the repulsion between positive charge of cadmium ion and the solid surface. As the solid surface donates a pair of nonbonding electrons,therefore, raising the amount of OH⁻ in the solution, and the pH of the solution trends to be higher. However, as shown in the fig.1 ,this tendency is no longer occurred when pH is higher than 4.This result is probably due to the solid

surface releases H$^+$,performing itself as Brønsted acid, (see equation (3) and (4)) into the solution resulting in the neutralization of H$^+$ and OH$^-$ and the constant of pH. This result agrees very well with the study by [2] , who found that pHs of the solution were not changed although the initial pHs of 4-10 were applied for this circumstance.

$$Al - OH \rightarrow Al - O^- + H^+ \qquad (3)$$
$$Si - OH \rightarrow Si - O^- + H^+ \qquad (4)$$
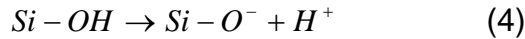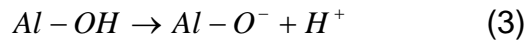
The second cause may be due to the competition between H$^+$ and Na$^+$ (see equation (5)) in which H$^+$ trends to replace Na$^+$ when pH of solution is low resulting in low cadmium ion removal efficiency and pH raising. [2]

$$NaZeolite + H^+ \rightarrow HZeolite + Na^+ \quad (5)$$
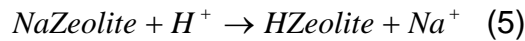
3.2 Effects of contact time and initial concentration

In this experiment, 1 ± 0.10 g of modified zeolite pellets (each formula) was put into the solution with cadmium ion concentration of 6, 16, 26, 35, 50, 65 and 100 mg/l (30 ml), and pH of the mixtures was kept at 4. After that, the mixtures were then shaken at 200 rpm. When each contact time was reached, the solution was separated by vacuum filtration. The cadmium concentration in the supernatant was then measured. Table 2 showed results of the experiment.

Table 2 Effect of initial concentration on contact time, adsorption capacity and removal of Cadmium with each modified pellet formula

| Initial conc.(mg/l)	Pellet 0P			Pellet 5P			Pellet 10P			Pellet 15P		
	Contact time(min)	Adsorption capacity (mg/g)	% remove	Contact time(min)	Adsorption capacity	% remove	Contact time(min)	Adsorption capacity	% remove	Contact time(min)	Adsorption capacity	% remove
6	900	0.22	98.9	900	0.19	97.4	900	0.21	96.8	900	0.19	98.7
16	900	0.52	99.4	900	0.45	98.5	900	0.49	97.9	900	0.46	99.2
26	900	0.81	99.3	900	0.71	98.5	1200	0.78	98.7	900	0.72	99.2
35	900	1.06	99.5	900	0.95	98.7	900	1.06	98.2	900	0.99	99.9
50	1200	1.59	99.6	900	1.37	98.3	1500	1.55	98.8	1200	1.38	99.6
65	900	2.07	99.1	1500	1.80	99.2	1500	1.98	99.0	1500	1.80	99.7
100	1500	3.14	99.8	1500	2.73	99.2	1500	3.06	98.1	1500	2.74	99.3
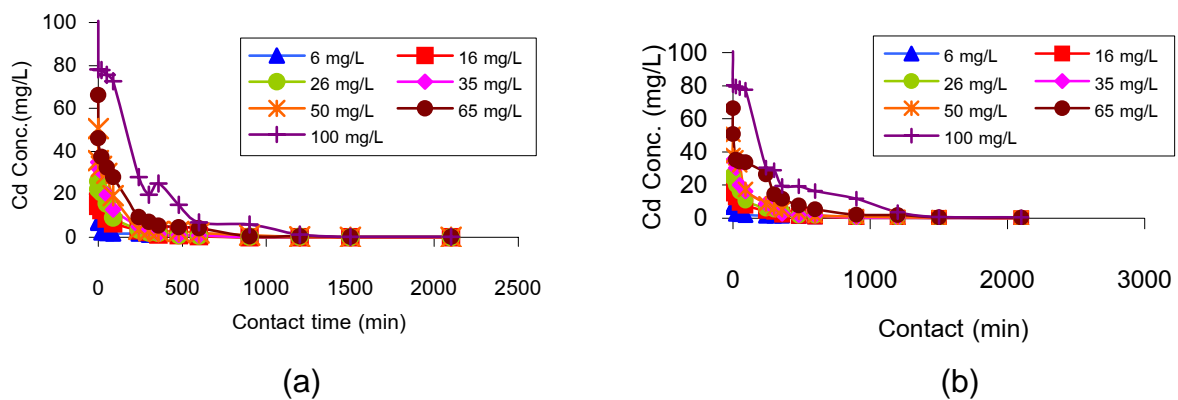
Fig.3 Effect of Contact time and initial concentration on removal of Cadmium with modified pellet 0P (a) and 5P (b).
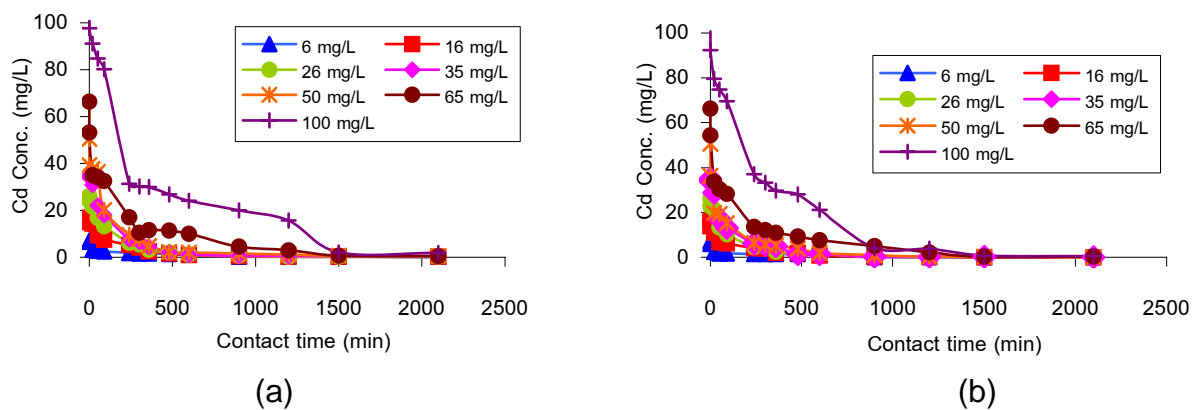

Fig.4 Effect of contact time and initial concentration on removal of Cadmium with modified pellet 10P (a) and 15P (b).

From fig. 3 and 4, at the lower initial concentrations (up to 50 mg/l), times to reach the equilibrium were around 900 minutes for all formulas. At the higher initial concentrations (65-100 mg/l), however, times to reach the equilibrium were higher and they were around 1500 minutes. These results were the evidences that contact time was affected by initial concentration. Moreover, contact times were almost the same for all formulas.

Due to the initial concentration affects the adsorption rate, at the first 240 minutes of agitation, removal efficiencies for all formulas were increased sharply (more than 60 %) and then increased slowly until the equilibrium were reached.

Moreover,these results showed that adsorption capacity was raised when initial concentration was increased. This may be due to more chances for pellet contacting at the higher concentration.The different in initial concentrations did not affect removal efficiency at equilibrium.In addition, the removal efficiencies for all formulas were almost the same and laid between 98-99 %, and the adsorption capacities for all modified zeolite pellet were lower than those values from different low cost

adsorbents such as chitosan (250 mg cd^{+2} /g), Chabazite (6.7-137 mg cd^{+2} /g), Clinoptilolite (3.7-70 mg cd^{+2} /g) and F-400 activated carbon (8 mg cd^{+2} /g).[3]

3.3 Isotherm Study

The adsorption data was fitted to the Langmuir (Eq.(6)) and the Freundlich (Eq.(7)) models using the linear regression analysis.For Langmuir adsorption isotherm can be represented by the expression

$$X/M = \frac{abc_e}{1 + bC_e} \qquad (6)$$

When Ce is equilibrium concentration of adsorbate in solution.The constant a is the Langmuir equilibrium constant and ab gives the theoretical monolayer saturation capacity.

For Freundlich adsorption isotherm can be represented by the expression:

$$X/M = KC_e^{1/n} \qquad (7)$$

When K is a Freundlich constant and 1/n is the Freundlich exponent. Table 3 shows the isotherm constant and theoretical adsorption capacity of pellet along with linear R^2 coefficient.

Table 3 Langmuir and Freundlich adsorption isotherm for cadmium removal with each modified pellet formula

Pellet	Adsorption Model	Model Constant	Adsorption Capacity (mg/g)	R^2
0P	Freundlich	K = 15.85 n = 1.00	1582.52	0.9823
	Langmuir	a = 0.94 b = 17.76	0.94	0.9944
5P	Freundlich	K= 3.91 n = 1.12	240.38	0.9681
	Langmuir	a = 0.79 b = 7.06	0.78	0.9763
10P	Freundlich	K = 2.49 n = 1.27	95.03	0.9361
	Langmuir	a = 0.56 b = 7.20	0.56	0.9850
15P	Freundlich	K = 6.38 n = 1.16	337.12	0.9326
	Langmuir	a = 0.77 b = 12.67	0.77	0.9768

The values of linear R^2 coefficient were high (> 0.9) for both isotherm indicating the useful values of its constants. However, due to Langmuir isotherm showed better fitted (higher R^2), so it was more appropiate than Freundlich isotherm in describing the adsorption process and although this study couldn't be exactly identified

mechanisms for removing cadmium ion by the pellet but theoretical basis of Langmuir isotherm assume all of accessible sites have the same energy, therefore, it could be implied that predominant mechanisms for this might be the adsorption and ion exchange rather than surface complexation or metal precipitation. [1]

In this experiment, however, some parts of pellet were broken down and suspended in the solution after agitation.Due to shear stress was created in solution. This problem led to find relationship between broken amount of pellets and agitation time, and results showed in the fig. 5
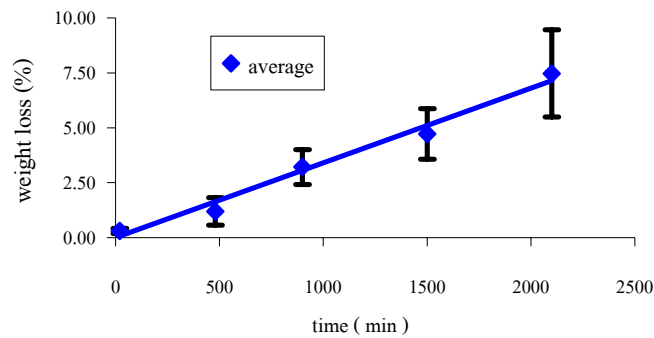

Fig.5 Effect of agitation times on the loss of average pellet weight due to its braking down during agitation by error bar represent 95% confidence limit

Table 4 Comparison some characteristics of each modified zeolite pellet with weight loss (due to braking down after agitation 2100 min.)
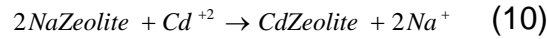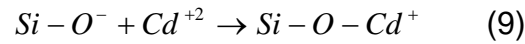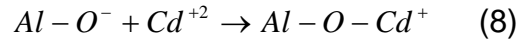
Pellet	CEC (meq./g.)	BET (sq.m./g.)	Adsorption Capacity(mg./g.)	% Wt. Loss (after 2100 min)
0P	0.28	8.37	0.944	8.8
5P	0.25	11.88	0.785	6.9
10P	0.35	10.45	0.555	6.1
15P	0.55	28.68	0.766	6.7

From fig.5, it is clearly indicated high correlation between the loss of average pellet weight due to its braking down and agitation time at initial pH of 4 ($R^2 > 0.97$). some characteristics of each modified zeolite pellet were compared with percent of weight loss due to its braking down are listed in table 4.These values were used to selected a modified zeolite pellet formula which suitable for column study.

Even though the sequence of pellet's adsorption capacity is 0P>5P>15P>10P which are the same as percent loss due to its braking down. And this can be implied that some parts of pellet which were broken down and suspended in the solution resulted in increasing adsorption capacity following increasing a chance for contacting between adsorbent and adsorbate. However, zeolite media used in column study are fixed, thus, less amount of zeolite pellet are broken apart and the braking effect to its capacity are negilable. For these reasons, the 15 P formula was selected to be used in the column study.

For the pH of solution after finished contacting for all initial cadmium concentrations, which was raised when contact time increased, and final pH was around 8-9 at

contact time of 2500 minute. At the pH of solution around 8-9, the main species of cadmium ion are Cd^{+2} (>90%) and $CdOH^+$(<10%).[4] The changes of species of cadmium ion and the change of surface chemistry of zeolite at pH of 8-9 as discussed previously lead to the assumption that the main mechanism for cadmium ion removal are adsorption and ion exchange as shown in Eq. (8) (9) and(10).[2]

$$Al - O^- + Cd^{+2} \rightarrow Al - O - Cd^+ \quad (8)$$
$$Si - O^- + Cd^{+2} \rightarrow Si - O - Cd^+ \quad (9)$$
$$2 NaZeolite + Cd^{+2} \rightarrow CdZeolite + 2Na^+ \quad (10)$$

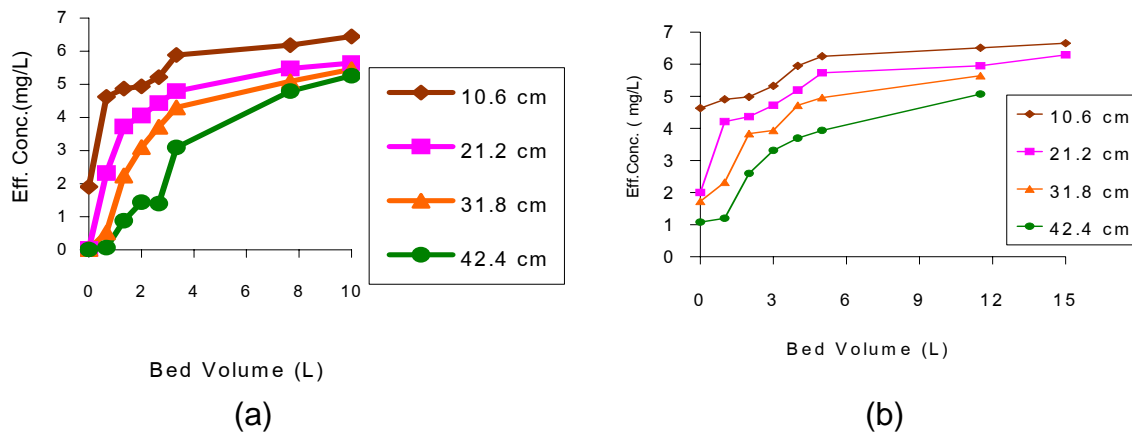## 3.4 Breakthrough curve of column in series

Fig. 6 Effect of various bed depths at a flow rate of 3.75 (a) 5.63 (b) cu.m./(sq.m.-hr.) in a fixed-bed column

In this study crushed zeolites pellets 15P were filled into four acrylic column that were connected in series. The column had the inside diameter of 1.9 cm and the bed depth of each column was 10.6 cm. The synthetic wastewater had cadmium ion concentration of 6.6 mg/l and pH of 4 and was fed into the column with the hydraulic loading rates of 3.75 and 5.63 m^3/m^2-hr.The effective size (D_{10}), Mean size (D_{50}) and Coefficient of uniformity of crushed zeolites pellet were 1.15 , 1.80 and 1.67 mm respectively. Results of the experiment were shown in fig. 6 and table 5

Table 5 Some result of column study.

HLR (cu.m/(sq.m-hr)	EBCT (min)	D (cm.)	Wt (g)	V_b (L)	Usage (g/l)
3.75	1.70	10.6	26.56	0.18	145.88
	3.39	21.2	53.12	0.82	64.77
	5.09	31.8	79.68	1.64	48.44
	6.78	42.4	106.24	3.16	33.64
5.63	2.26	21.2	53.12	0.29	182.66
	3.39	31.8	79.68	1.21	65.66
	4.52	42.4	106.24	2.07	51.36

From fig.6 and table 5 showed that V_b which means volume at a point which lower edge of mass transfer zone MTZ reaches the bottom of the column which is called breakthrough point , increased with decreasing HLR ,due to the longer contact time (EBCT) , or increasing bed depth while the shape of breakthrough curves were slightly different at the same HLR.

According to Bohart-Adams model, Bed depth-service time (BDST) plots in which service time, T_b is plotted versus bed depth, D and can be represented by the expression:

$$T_b = \frac{N_o}{C_o V}\left[D - \frac{V}{KN_o} \ln\left(\frac{C_o}{C_n} - 1 \right) \right] \quad (11)$$

The adsorptive capacity of system, N_o, and the rate constant, K can be evaluated from slope and intercept respectively. L_{MTZ} can be calculated from Eq.11 by letting $T_b = 0$ and solving for D. BDST curves were shown in fig. 7 and some BDST constants were shown in table 6
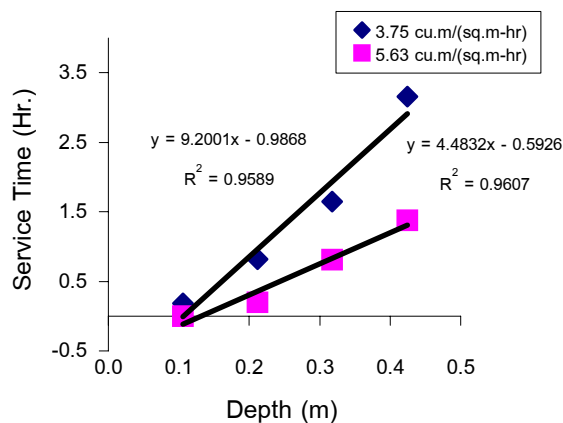

Fig. 7 Relation between bed depth and service times at 40% breakthrough at 3.75 and 5.63 cu.m/(sq.m-hr)
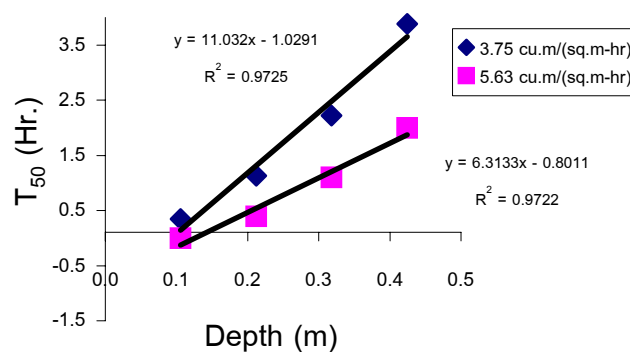

Fig. 8 Relation between bed depth and service times at 50% breakthrough at 3.75 and 5.63 cu.m/(sq.m-hr)

Table 6 Some Bohart-Adams model constants for column study.

HLR (cu.m/(sq.m-hr))	L_{MTZ} (cm)	N_0 mg/l	K (l/(mg-hr))	X (mg/g)
3.75	10.7	0.23	0.0621	0.26
5.63	13.2	0.17	0.1034	0.19

From table 6 showed that the adsorptive capacity of system, N_o was calculated to be 0.23 and 0.17 mg/l for 3.75 and 5.63 (cu.m/(sq.m-hr)) respectively.This indicates that N_o or X may increase with decreasing HLR or increasing EBCT. And for the amount of cadmium retained by zeolite, X was at range 0.19 - 0.26 mg/g and lower than in batch study which was approximately 0.76 mg/g for modified zeolite pellet 15P by using Langmuir model (see table 3).This show that in the column study, although, the zeolite pellet was crushed for filling into column and has unit weight approximately less than that of batch study but it may not provide better contact between adsorbent and adsobate than that of batch study that may be due to the flow disturbances, channeling effects in column lead to non equilibrium stage in the column system. [5]

By contrast, L_{MTZ} which means a sufficient length of mass transfer zone to attain a satisfactory effluent as 40% breakthrough concentration for this study increased with increasing HLR mean that the mass transfer zone must be increased to remove cadmium under the higher flow rate or HLR.

At 50% breakthrough,if the BDST curve is a straight line passing through the origin,the adsorption data follow the BDST model due to logarithmic term in Eq. 11 reduces to zero [6], giving the relationship as Eq. 12:

$$T_{50} = N_O D /(C_0 * V)   (12)$$

From fig. 8 ,although these curves ae not pass through the origin but the relationship between service time and bed depth could be investigated for pilot system design that express in Eq. 13 and 14:

$$T = 9.2001D - 0.9868 (R^2 = 0.9589)   (13)$$
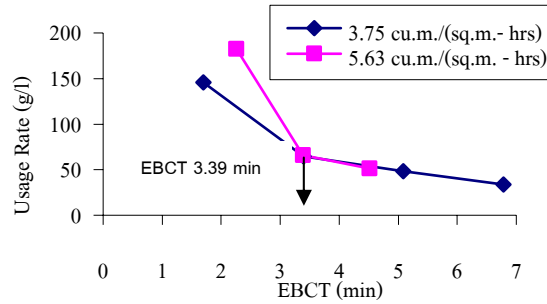$$T = 4.4832D - 0.5926 (R^2 = 0.9607)   (14)$$

Fig. 9 Usage rate of crushed zeolite pellet 15P versus EBCT

In addition, the flow rate represents the EBCT in the column, which affects the volume to breakthrough and the shape of breakthrough curve. EBCT can be represented by the expression:

$$EBCT = bed\ volume/flow\ rate \qquad (15)$$

From table 5, the crushed zeolite pellet usage rate ,represented the volume to breakthrough per crushed zeolite pellet unit weight, was plotted versus EBCT as shown in fig. 9 that usage rate was reduced when EBCT was increased (corresponding to longer bed depth). After at EBCT 3.39 minutes, both curves flatten and no significant reduction in usage rate and this EBCT at lowest usage rate would use for pilot system design by the optimum EBCT should not be less than 3.39 minutes to maintain mass transfer zone at this lowest usage rate. This can be explained that when EBCT increase, bed life or service time will increase due to the effects of advection and axial dispersion are reduced as flow pattern approach ideal plug flow. Consequently, the shape of breakthrough curve should be similar to the invert L-shape. Hence, the increasing rate of the volume to breakthrough reduced, resulting in less variation of usage rate. [7]

Therefore, Eq.16 and 17 used for determining the EBCT at known crushed zeolite pellet usage rate with the hydraulic loading rates of 3.75 and 5.63 m^3/m^2-hr. respectively.

$$Usage\ rate = 245.98EBCT^{-1.034} \quad (R^2 = 0.9923) \quad (16)$$
$$Usage\ rate = 780.24EBCT^{-1.8759} \quad (R^2 = 0.9425) \quad (17)$$

4. Conclusions

The present study examined the use of modified zeolite pellet which were developed as different four pellet formulas in previous study, for the removal of cadmium from aqueous solution.The optimum pH was found to be 4.0. For batch study, residual cadmium concentration reached equilibrium in 1500 min and the removal efficiency were more than 98% in all formula of modified zeolite pellet and initial concentration. Isotherm analysis of the data showed that the adsorption pattern for cadmium on modified zeolite pellet followed the Langmuir model which the maximum capacity of 3.14 mg/g. and are much lower than other low-cost adsorbents.

For column study as series application was investigated. According to Bohart-Adams model, the adsorption capacity was 0.26 and 0.19 mg/g. for HLR at 3.75 and 5.63 $m^3/(m^2\text{-}hr)$.,respectively by using initial cadmium concentration 6.6 mg/l. of synthetic wastewater. This showed that the lower HLR or upper bed depth would have higher volume to breakthrough due to an increase in EBCT and to maintain mass transfer zone at this usage rate , optimum EBCT should not be less than 3.39 min.

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Nomenclature

C_e equilibrium concentration of adsorbate in solution (mg/l)

a the Langmuir equilibrium constant

ab the theoretical monolayer saturation capacity.

K Freundlich constant

$1/n$ Freundlich exponent

BDST   bed depth service time

EBCT   empty bed contact time

T_b service time (hr)

D bed depth (cm)

HLR   hydraulic loading rate (cu.m/(sq.m-hr))

N_o the adsorptive capacity per volumn of bed (mg/l)

K the rate constant (l/(mg-hr))

L_{MTZ} the length of mass transfer zone (cm)

T_{50} time required for the effluent to reach 50% breakthrough concentration (hr)

V_b volume of breakthrough (l)

V linear flow rate through the bed (cm/hr)

Wt   weight of adsorbent in column (g)

X   amount of Cd loaded on the adsorbent per mass of adsorbent (mg/g)