CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of the fired clay chips

In order to understand the ability of fired clay material in removing the fluoride, the fired clay chips with 4-20 mesh size was characterized on its physical adsorption properties and its chemical compositions. The characteristics including chemical composition, surface area, pore volume distribution and pore radius are shown in Table 3.1

Table 3.1 Physical and chemical properties of fired clay chips

Physical properties		**Chemical compositions**	**(% wt)**
Surface area	4.23 m^2/g	SiO_2	66.07
Pore volume distribution	0.024 ml/g	Al_2O_3	19.84
Pore radius	83.5 Å	Fe_2O_3	6.22
		TiO_2	0.42
		CaO	0.09
		MgO	1.13
		Na_2O	0.84
		K_2O	4.02

According to its chemical compositions, the major components which comprise SiO_2, Al_2O_3 and Fe_2O_3 should play an important role on fluoride removal based on the adsorption process. This is because these three oxides are best known as good adsorbents. It is thus expected that fluoride will be mostly adsorbed either by any composition or by a combined influence of the major oxides present in the adsorbent. Considering the physical characteristic of the fired clay chips with 4-20 mesh size, it has average surface area of 4.23 m^2/g, 0.024 ml/g of pore volume distribution and pore radius of 83.5 Å. The physical characteristics of fired clay chips shows moderate surface area and pore volume distribution for fluoride adsorption when compared with fired brick [30]. They were anticipated that fluoride ion will be adsorbed on the surface or in the cavity of fired clay chips. As for the reason that the fired clay chips have moderate distribution of surface area and pore volume when compared with fired brick, probably due to the different in raw materials and production step. The fired clay chips is made from clay and water which fired at high temperature (1300-1600°C) but the raw materials for fired brick chips production are clay, water, rice husks and saw dust which are fired at low temperature (900-1200 °C).

3.2 Performance evaluation of the fluoride ion selective electrode and construction of the fluoride calibration curve

Evaluation of the performance of fluoride ion selective electrode was necessary in order to ensure good accuracy and precision of the experiment. The performance of this electrode was evaluated from the slope of the fluoride calibration curve. The calibration curve of standard fluoride solution was established by plotting the logarithmic concentration of the fluoride and its corresponding potential of the measurement. In this work, the calibration curve of standard fluoride solutions with concentration ranging from 1, 2, 3, 4 and 5 mg/l were studied. Each standard fluoride solution was measured potentiometrically by using fluoride ion selective electrode. The results are presented in Table 3.2 and Figure 3.1

Table 3.2 Logarithm of the concentration and the voltage of standard fluoride solution

Concentration of standard fluoride solution, mg/l	Logarithm of fluoride concentration	Voltage, mV
1.00	0.000	140
2.00	0.301	123
3.00	0.477	112
4.00	0.602	105
5.00	0.699	99

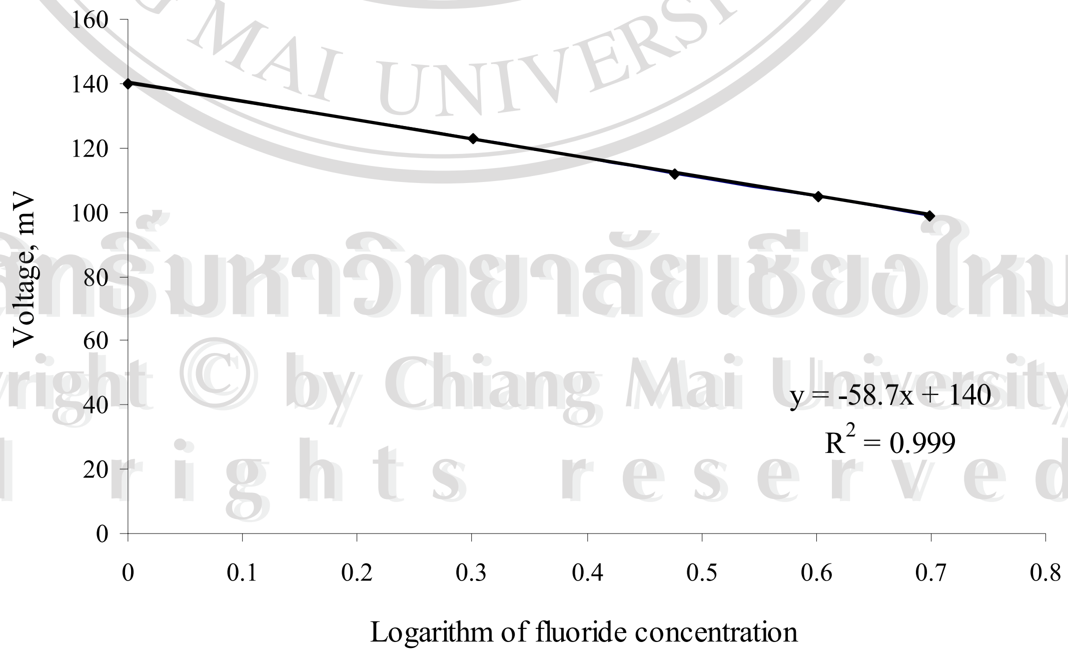

Figure 3.1 Calibration curve of the standard fluoride solution

From the standard fluoride calibration curve, the slope value is 58.7 mV. The electrode is regarded as being in a good operating condition, if the slope of the fluoride calibration curve changes within 57 ± 2 mV [32]. Therefore, this value confirms good precision and accuracy of the fluoride ion selective electrode. In Addition, the linearity of standard fluoride curve is reflected by the R^2-value of which equals to 0.999, therefore this demonstrates an extremely good response of the electrode being in use.

3.3 The study of fluoride adsorption onto fired clay chips

In order to understand the nature of fluoride adsorption onto fired clay chips, all adsorption experiments were designed and carried out batchwise. Parameters affecting the adsorption such as the size of fired clay chips, static and dynamic conditions, agitation rate, contact times, initial fluoride concentration, pH, temperature and coexisting ions were optimized and the results obtained are as follows.

3.3.1) Effect of the particle size of fired clay chips

A preliminary screening study was conducted to assess the influence of particle size of fired clay chips for fluoride removal. The sizes of fired clay chips were varied from 20- <1 mesh. The results are illustrated in Table 3.3

Table 3.3 Effect of the particle size of fired clay chips on fluoride adsorption

Particle size, mesh	Specific amount of adsorbed fluoride, μmol/g
4-20	0.187
1-4	0.126
<1	0.102

It is obviously shown that the amount of adsorbed fluoride increases with a decrease of the particle size of fired clay chips. The adsorption of fluoride on small size particles is significantly greater than on large size particles. This may be due to the increase of adsorbent surface area and pore volume distribution.

3.3.2) Effect of the dynamic and static conditions

The fluoride adsorption on fired clay chips was studied under two different conditions, dynamic and static in order to compare the equilibration methods. For the dynamic condition, shaking with a shaker machine at 150 rpm at the time interval of 0.5, 1.0, 2.0, 2.5 and 3.0 hours resulted in quite a different uptake capability of the fired clay chips compared with that of the static one. The numerical results are shown in Table 3.4 and Figure 3.2

Table 3.4 Residual fluoride concentration at static and dynamic conditions

Time, hrs	Residual fluoride concentration, mg/l	
	Static condition	**Dynamic condition**
0.0	5.00	5.00
0.5	4.83	3.79
1.0	4.70	3.10
1.5	4.65	2.65
2.0	4.52	2.57
2.5	4.46	2.44
3.0	4.41	2.41

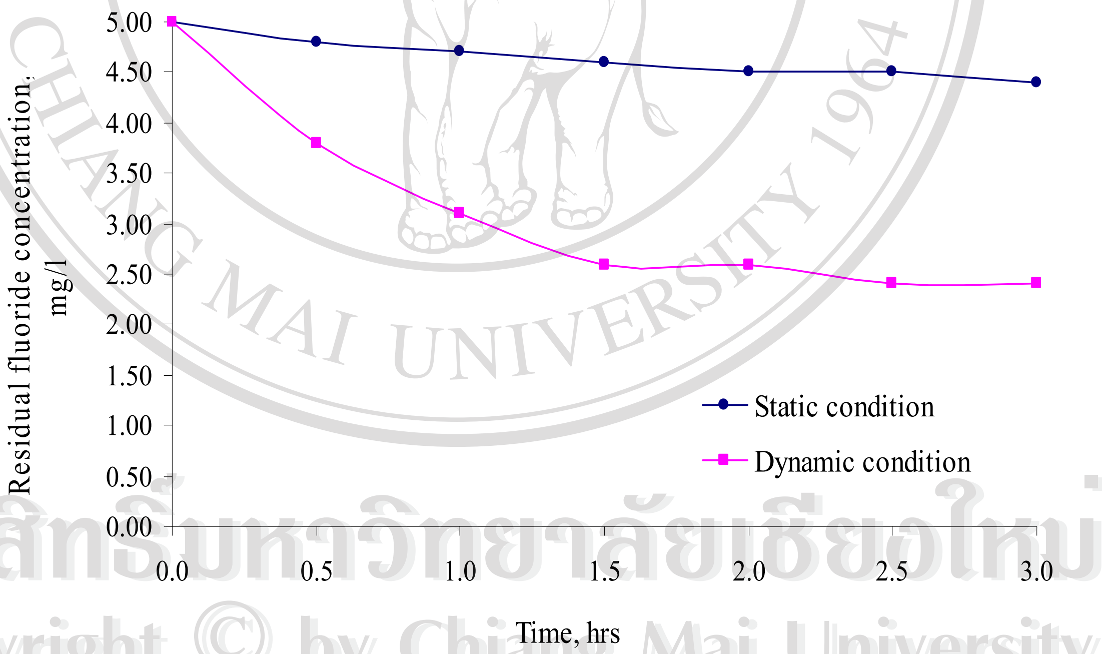

Figure 3.2 Effect of the static and dynamic conditions on fluoride adsorption

From the figures in Table 3.4, it was found that almost 50% of fluoride ions in a bulk solution was reduced within 2 hours with agitation, but under a static condition only 12% of fluoride was removed. When compare the rate of fluoride adsorption at any times between static and dynamic conditions, it is evidently clear that the fluoride removal occurs in much faster fashion under the dynamic condition. The concentration of residual fluoride was found to decrease within an hour and a half, then its decrease turns out to be very slightly afterward. The results obtained from this study are quite obvious due to the fact that agitation causes the movement of ions within system. At the same time, the adsorbent particles always move around within the solution. Such a movement will, for sure, enhance the adsorption of fluoride ions onto the surface of fired clay chips because the mass transfer of both fluoride and fired clay chips is increased. Thus, the dynamic condition was used to study the fluoride adsorption in the experiment.

3.3.3) Effect of the agitation rates

Considering the results from studying the effect of static and dynamic conditions on fluoride adsorption, it was found that the dynamic condition provided a higher efficiency for defluoridation. Thus, the optimum agitation rate providing the best adsorption was studied. The results of the variations of the agitation rate are presented in Table 3.5 and Figure 3.3

Table 3.5 Residual fluoride concentration at different agitation rates

Agitation rate, rpm	**Residual fluoride concentration, mg/l**
50	2.45
100	2.41
150	2.44
200	2.54
300	2.79
400	2.81
500	2.85

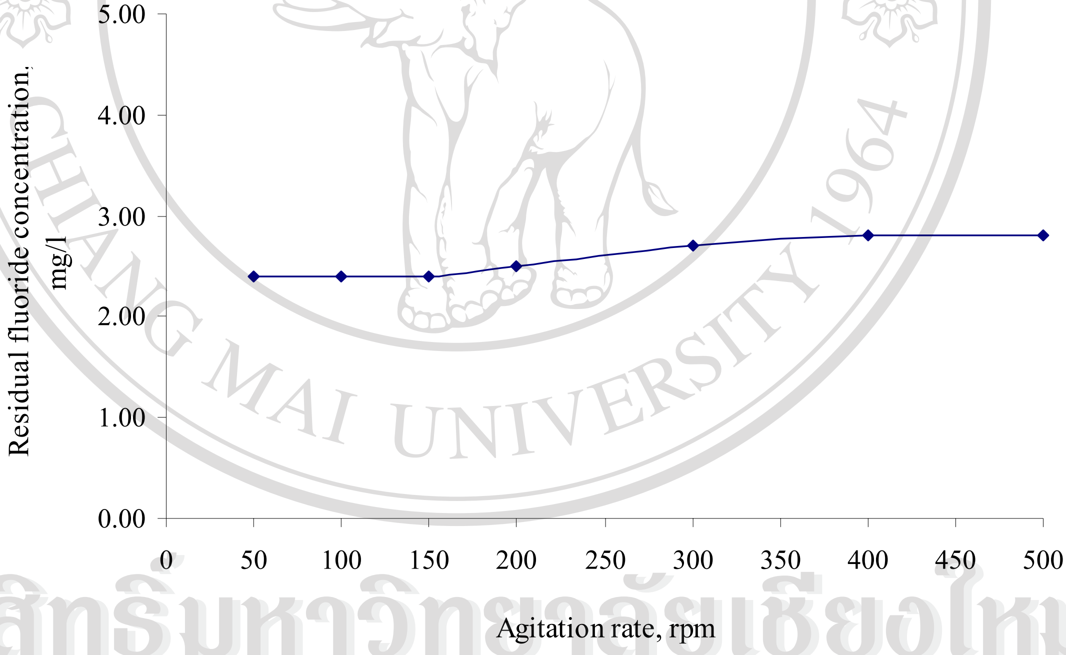

Figure 3.3 Effect of the agitation rate on fluoride adsorption by fired clay chips

The variation in the adsorption of fluoride as a function of agitation speed was studied using 5 mg/l fluoride solution with 20 g of fired clay chips. The effect of agitation rate was expressed as the rotational speed of the impeller. It appeared that the adsorption rate at higher agitation speed tended to be slower than lower agitation speed. By considering the movement of shaker machine, the shaker was rotated in 360 degree. Thus, during the shaking process the movement of mixture solution was in a vortex fashion. Therefore, at fast agitation rate, the fluoride ion in the bulk solution cannot be adsorbed on the bare surface of fired clay chips, efficiently due to the centrifugal action. In addition, the fast movement of the ions prohibits the penetration of ions into the pore of fired clay chips causing a decrease in adsorption.

3.3.4) Effect of the contact time and initial fluoride concentration

The effect of contact time and initial fluoride concentration on fluoride adsorption were studied on fired clay chips. The main fraction of 4-20 mesh size was used throughout for the study. The adsorption experiments were carried out by equilibrating the fluoride solution of different initial concentrations with appropriate amount of fired clay chips at different contact times. At different time intervals, sample was analyzed for the residual fluoride concentration using fluoride ion selective electrode. The results obtained were shown in Table 3.6 and Figure 3.4

Table 3.6 Fluoride adsorption in relation with contact times at different initial fluoride concentrations

Contact time, hrs	**Specific amount of adsorbed fluoride, µmol /g**		
	5 mg/l initial concentration	**10 mg/l initial concentration**	**20 mg/l initial concentration**
0.5	0.093	0.205	0.364
1.0	0.145	0.333	0.685
1.5	0.180	0.379	0.749
2.0	0.192	0.412	0.787
2.5	0.196	0.411	0.783
3.0	0.199	0.411	0.777
3.5	0.200	0.417	0.786
4.0	0.205	0.411	0.792
4.5	0.201	0.422	0.796
5.0	0.218	0.415	0.794

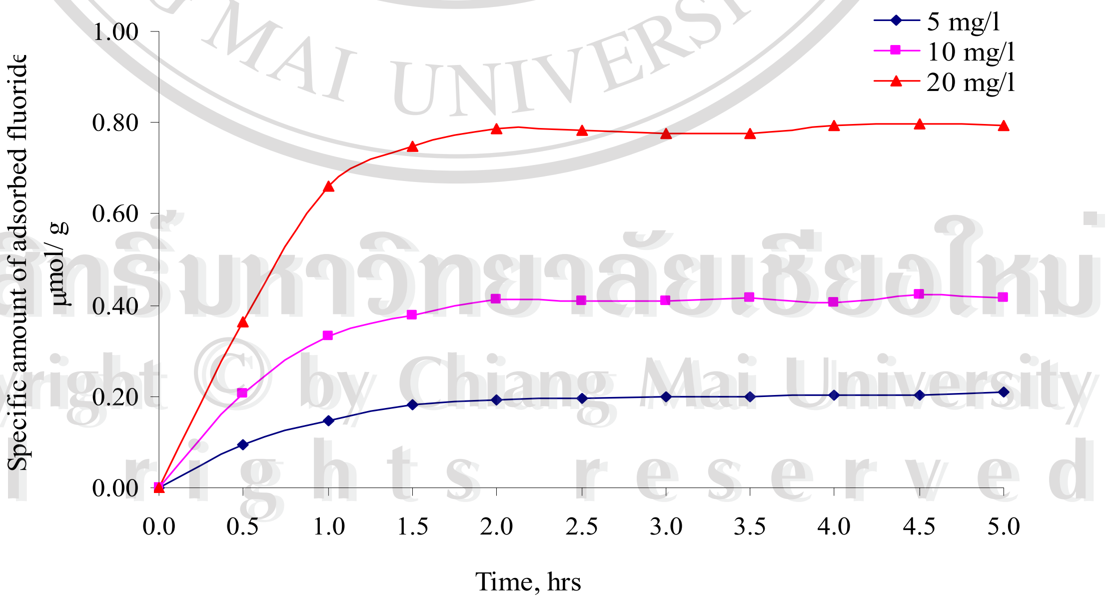

Figure 3.4 Time-dependent adsorption profile of fluoride on fired clay chips at different initial concentrations of fluoride

Table 3.6 and Figure 3.4 showed the variation of fluoride concentration at different contact times when the initial concentrations of fluoride were varied. It can be seen that with the fixed amount of fired clay chips, the amount of fluoride adsorbed increases with time as well as the initial concentration and reaches equilibrium conditions in approximately 2 hours of contact. The time to reach equilibrium conditions appears to be independent of initial fluoride concentration. This probably due to the adsorption site of adsorbent (a constant amount for various initial fluoride concentrations) were exhausted in almost the same time. The overall amount of fluoride adsorbed at 2 hours for different initial fluoride concentrations of 5, 10 and 20 mg/l are 0.19, 0.41 and 0.79 μmol/g, respectively. This can be indicated that for a given size and amount of the adsorbent, the amount of solute adsorbed per gram of the adsorbent increases with increase of initial fluoride concentration. It might be due to a greater driving force from the mass action process which results in more adsorption at a higher fluoride concentration.

3.3.5) Effect of the pH

The pH of the aqueous solution is an important variable which controls the adsorption at the water-adsorbent interfaces. This study was to investigate the effect of pH at different pH-values ranging from 3-9 on fluoride adsorption by fired clay chips. The experiment was performed at room temperature on 4-20 mesh fired clay chips when the fluoride concentrations were varied from 5 to 30 mg/l. The residual fluoride remained in the solution was determined potentiometrically. The results of the study are shown in Table 3.7 and Figure 3.5

Table 3.7 The residual fluoride concentration and the amount of disappeared fluoride at different pH

Initial fluoride concentration, mg/l	pH	Equilibrium fluoride concentration, mg/l	Specific amount of disappeared fluoride, μmol/g
5.00	3	1.55	0.276
	4	1.61	0.264
	5	2.04	0.200
	6	2.47	0.197
	7	2.53	0.196
	8	2.57	0.187
	9	2.63	0.184
10.0	3	2.60	0.566
	4	317	0.524
	5	5.18	0.369
	6	5.18	0.377
	7	5.06	0.386
	8	5.18	0.372
	9	5.39	0.360
20.0	3	5.70	1.10
	4	6.68	1.02
	5	10.9	0.708
	6	10.7	0.700
	7	10.6	0.719
	8	10.6	0.716
	9	10.7	0.705
30.0	3	8.35	1.65
	4	10.1	1.52
	5	15.8	1.09
	6	15.8	1.08
	7	15.3	1.12

Table 3.7 (continued)

Initial fluoride concentration, mg/l	pH	Equilibrium fluoride concentration, mg/l	Specific amount of disappeared fluoride, µmol/g
	8	15.7	1.07
	9	16.4	1.06

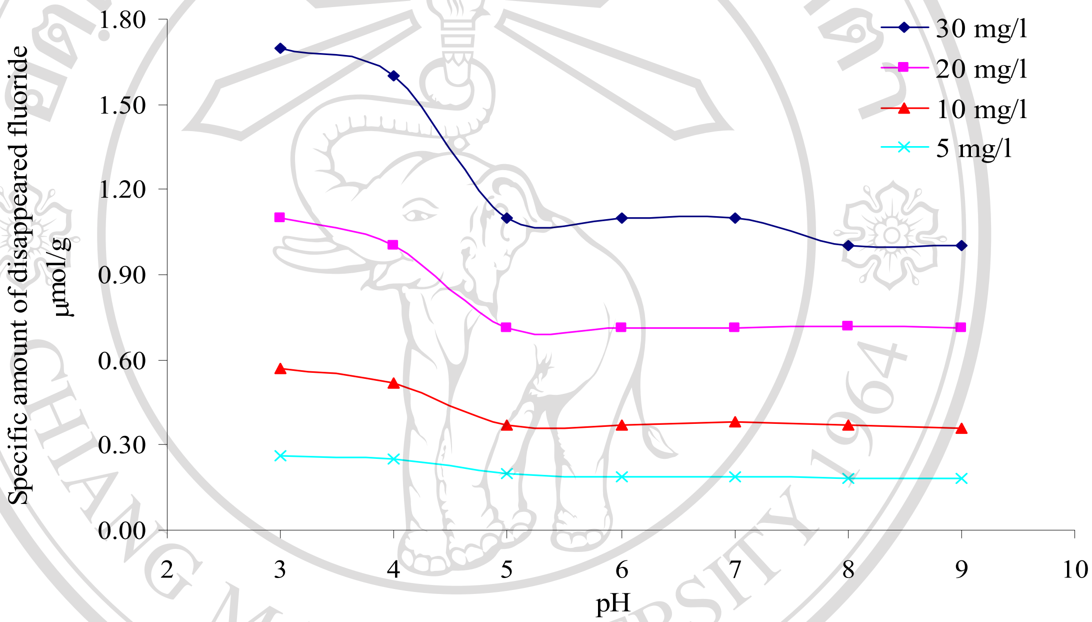

Figure 3.5 Effect of pH on the adsorption of fluoride by fired clay chips

The effect of pH of the solution on the performance of adsorbent was investigated by varying the pH ranging from 3-9 while keeping other parameters constant, such as particle size, agitation rate, adsorbent mass, contact time and fluoride concentration. The results are presented in Table 3.7 and Figure 3.5. It can be observed that the specific amount of disappeared fluoride is more in the pH range of 3 to 4. This result could mislead to the conclusion that fluoride ion was adsorbed in a greater extent at lower pH. The actual cause of the diminishing of fluoride in the bulk solution is the formation of HF_2^- and HF in the highly acidic medium. These ions could not be detected by fluoride ion selective electrode [24]. Thus, the residual fluoride concentration in the bulk solution is demonstrated to be less than what it should be if the disappearance of fluoride is due solely to adsorption. However, at the pH values of 5 to 9, there is no appreciable change in the amount of fluoride adsorbed onto the fired clay chips.

Therefore, it is concluded that, as the low initial fluoride concentration (5 and 10 mg/l), it reveals definitely that pH of fluoride solution posed slightly effect on the fluoride adsorption by fired clay chips compared to high initial fluoride concentration (20 and 30 mg/l). Thus, there is no need for pH adjustment in the study of fluoride adsorption.

3.3.6) Effect of the temperature

The effect of temperature on fluoride adsorption onto fired clay chips was studied at different temperatures i.e. 30, 40 and 50 °C. The experimental results are shown in Table 3.8 to 3.10 and Figure 3.6 to 3.9.

Table 3.8 Adsorption isotherm data at 30 °C

Initial fluoride concentration, mg/l	Equilibrium fluoride concentration, mg/l	Specific amount of adsorbed fluoride, μmol/g
5.00	2.55	0.184
10.0	5.79	0.327
20.0	11.7	0.643
30.0	17.3	0.962
40.0	25.6	1.10

Table 3.8 (continued)

Initial fluoride concentration, mg/l	Equilibrium fluoride concentration, mg/l	Specific amount of adsorbed fluoride, μmol/g
50.0	31.8	1.33
60.0	38.4	1.66
70.0	43.8	2.01
80.0	46.7	2.56
90.0	56.1	2.58
100	63.1	2.82
130	73.8	4.29
160	93.4	5.09
200	1.19×10^2	6.14
260	1.36×10^2	9.59
300	1.61×10^2	10.4

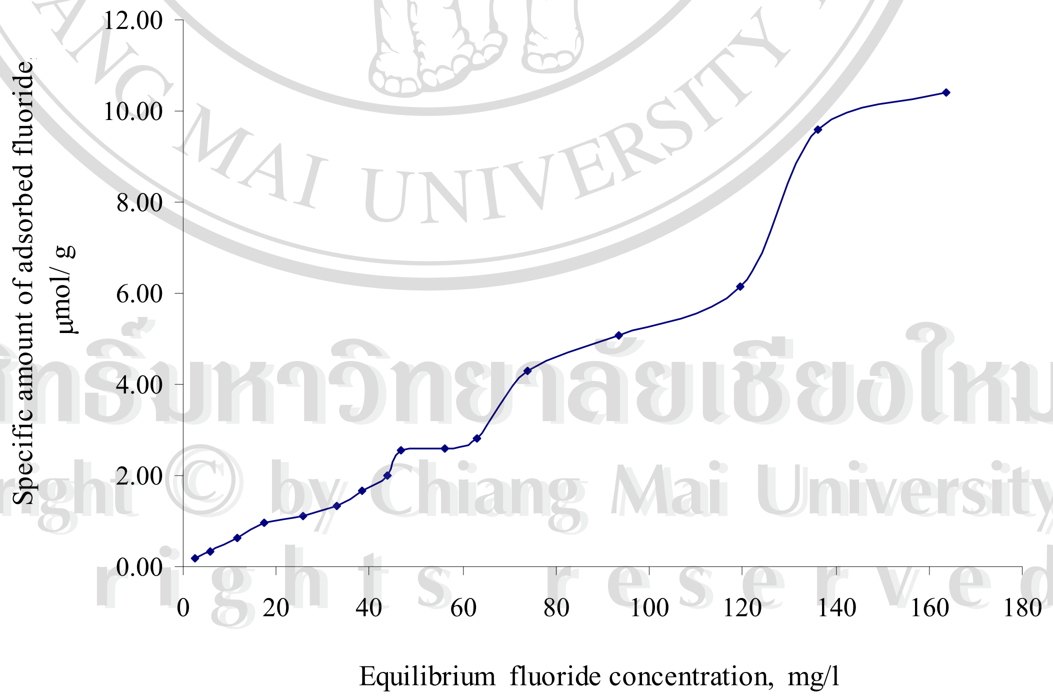

Figure 3.6 Adsorption isotherm of fluoride on fired clay chips at 30 °C

Table 3.9 Adsorption isotherm data at 40 °C

Initial fluoride concentration, mg/l	Equilibrium fluoride concentration, mg/l	Specific amount of adsorbed fluoride, μmol/g
5.00	2.48	0.193
10.0	5.53	0.334
20.0	11.2	0.677
30.0	17.2	0.983
40.0	25.4	1.11
50.0	32.1	1.37
60.0	38.5	1.71
70.0	42.2	2.14
80.0	45.1	2.67
90.0	54.8	2.71
100	62.3	2.88
130	70.1	4.63
160	93.3	5.15
200	1.14×10^2	6.16
260	1.29×10^2	9.98
300	1.51×10^2	10.9

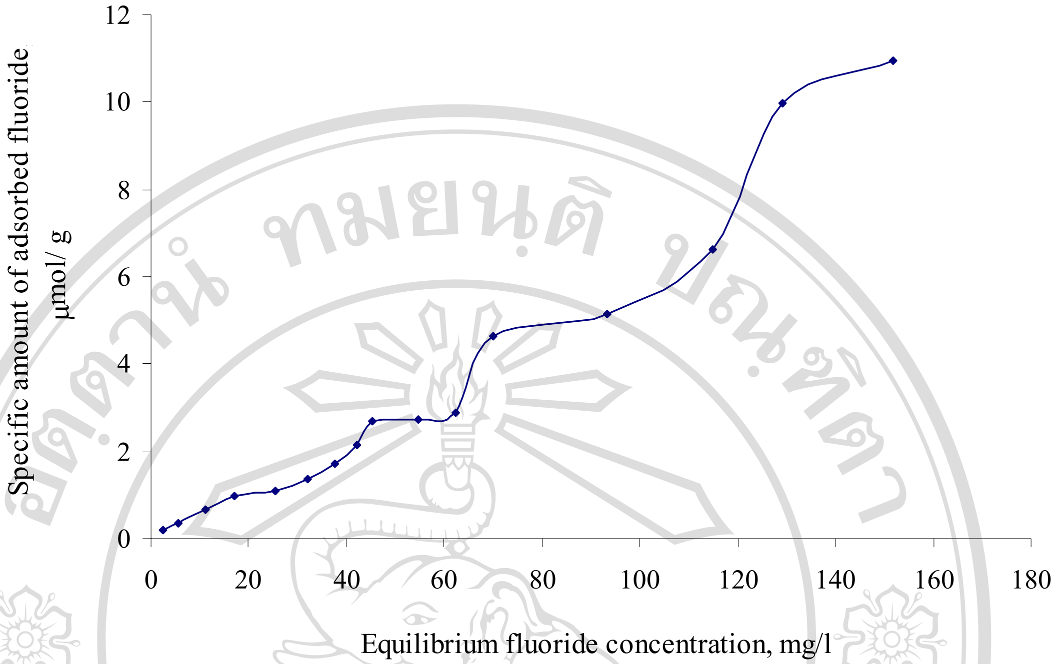

Figure 3.7 Adsorption isotherm of fluoride on fired clay chips at 40 °C

Table 3.10 Adsorption isotherm data at 50 °C

Initial fluoride concentration, mg/l	Equilibrium fluoride concentration, mg/l	Specific amount of adsorbed fluoride, µmol/g
5.00	2.44	0.200
10.0	4.98	0.388
20.0	10.5	0.730
30.0	16.7	1.02
40.0	25.3	1.12
50.0	29.6	1.58
60.0	34.6	1.96
70.0	38.6	2.46
80.0	40.6	3.04
90.0	45.2	3.42
100	55.3	3.46

Table 3.10 (continued)

Initial fluoride concentration, mg/l	Equilibrium fluoride concentration, mg/l	Specific amount of adsorbed fluoride, μmol/g
130	67.9	4.77
160	92.1	5.22
200	1.09×10^2	7.02
260	$1.2\ 3 \times 10^2$	10.6
300	1.49×10^2	11.5

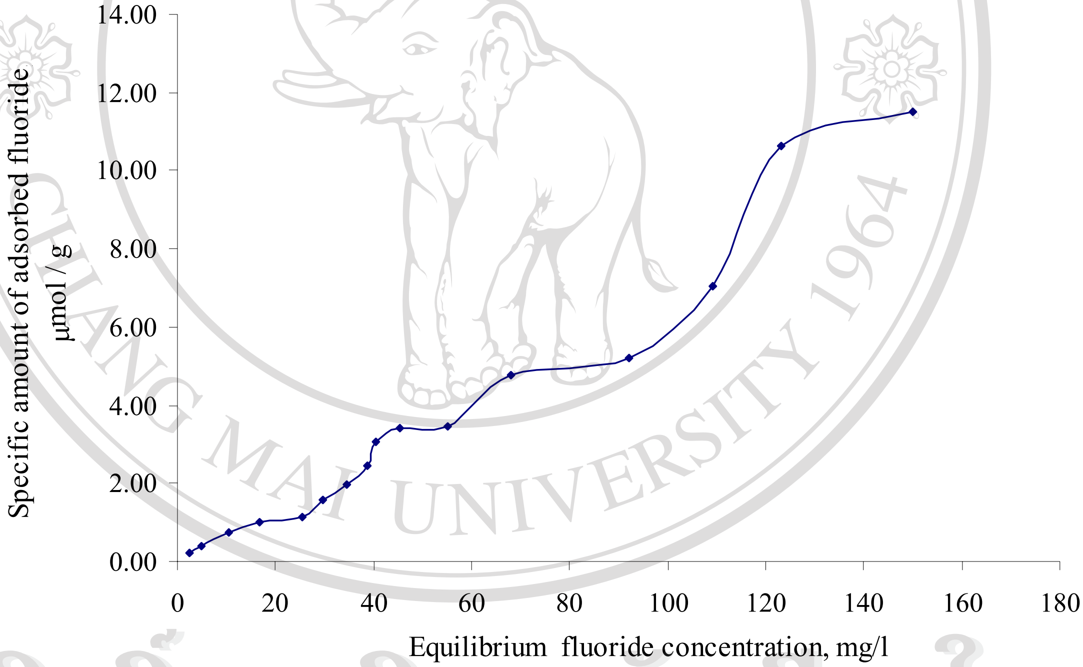

Figure 3.8 Adsorption isotherm of fluoride on fired clay chips at 50 °C

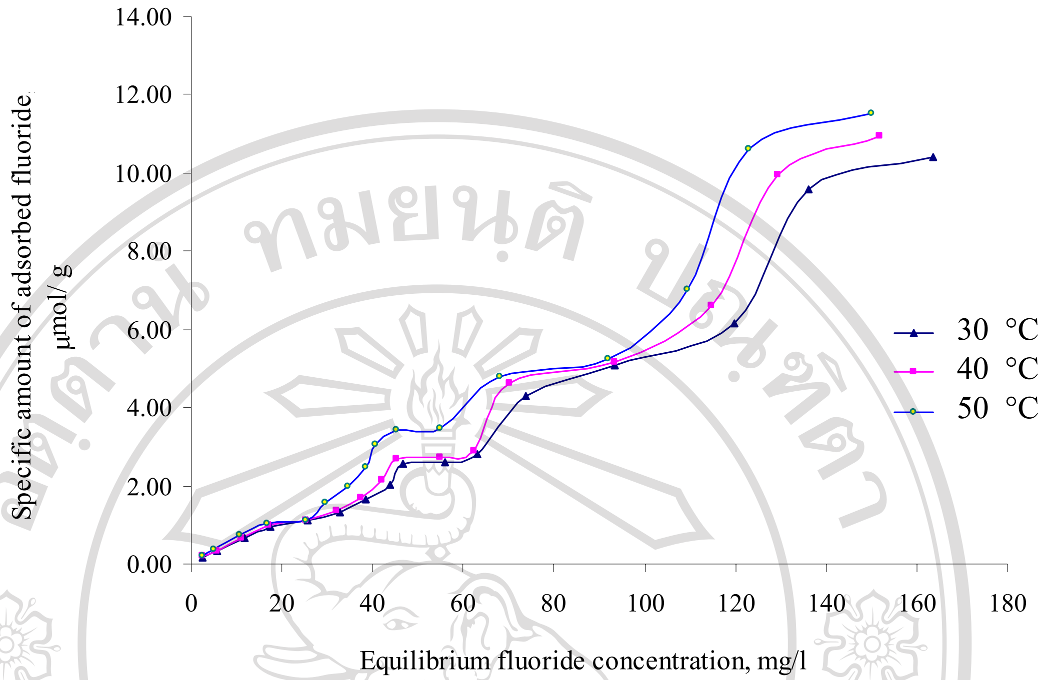

Figure 3.9 Adsorption isotherms of fluoride on fired clay chips at 30, 40 and 50 °C

For an increase in temperature from 30 to 50 °C on fluoride adsorption by fired clay chips, it was observed that the temperature of adsorption posed a slight effect on fluoride adsorption by fired clay chips. With the increase in temperature at various initial fluoride concentrations the amount of adsorbed fluoride was also increase. The enhancement of fluoride adsorption by fired clay chips with temperature is attributed to the possible increase in the kinetic effects. At higher temperature, the fluoride ions move faster and more fluorides can penetrate into the cavities of fired clay chips. Based on the adsorption isotherm of fluoride at various temperatures, if the first deflection point on the isotherm is regarded as the monolayer adsorption, the capacity of fired clay chips for fluoride adsorption at 30 °C will be about 0.95 µmol/g.

From adsorption isotherm, we can calculate the heat of adsorption or enthalpy of adsorption by using Clausius-Clapeyron equation. The heat of adsorption can be analyzed by plotting logarithm of the residual fluoride concentration at three different temperatures (30, 40 and 50 °C) versus the reciprocal of the temperature.

Table 3.11 Calculation for heat of adsorption of fluoride on fired clay chips

Temperature, °C	**Temperature, K**	**1/T, (× 10^{-3} K^{-1})**	**Equilibrium concentration, (× 10^{-3} M)**	**ln C**
30	303	3.30	0.912	-7.00
40	313	3.19	0.905	-7.01
50	323	3.10	0.883	-7.03

Figure 3.10 The relationship between Logarithm of the residual fluoride concentration and the reciprocal of temperature

From Figure 3.10, it is found that slope of the curve is 159. Thus, the heat of adsorption can be calculated by

$$\ln C = \frac{-\Delta H_{ads}}{RT} + k$$

$$\Delta H_{ads} = (159\ K)(8.314\ JK^{-1}mol^{-1})$$

$$= +1.321\ kJ/mol$$

From the calculated heat of adsorption which is +1.321 kJ/mol. The value is positive and less than 20 kJ/mol. So the adsorption of fluoride onto fired clay chips tends to be endothermic multilayer type. Moreover from the characteristic of the adsorption isotherm curve, it can be indicated that the adsorption of fluoride onto fired clay chips is not a monolayer type because the amount of adsorbed fluoride do not reach any saturation with the increase of initial fluoride concentration.

3.3.7) Effect of the coexisting ions

Drinking water usually contains many substances. These substances could interfere the adsorption of fluoride on fired clay chips. Thus, it would be worthwhile to study the effect of competitive ions like sulfate, phosphate, nitrate, chloride, sodium, potassium, iodide, calcium and magnesium. The results of this study are shown in Table 3.12 and Figure 3.11

Table 3.12 Residual fluoride concentration at different ratios of coexisting ions and fluoride ion

Coexisting ions	Residual fluoride concentration at different ratios of coexisting ion, mg/l							
	1:0	**1:1**	**1:10**	**1:25**	**1:50**	**1:75**	**1:100**	**1:150**
Ca^{2+}	2.66	2.49	2.46	2.43	2.37	2.37	2.34	2.31
Mg^{2+}	2.66	2.59	2.53	2.46	2.43	2.43	2.46	2.40
K^{+}	2.66	2.61	2.69	2.71	2.68	2.77	2.80	2.71
Na^{+}	2.66	2.69	2.71	2.69	2.71	2.77	2.81	2.77
SO^{2-}_4	2.66	2.73	2.77	2.77	2.80	2.77	2.80	2.80
PO^{3-}_4	2.66	2.70	2.77	2.80	2.88	2.84	2.77	2.84
NO^{-}_3	2.66	2.77	2.80	2.80	2.84	2.84	2.77	2.84
Cl^{-}	2.66	2.88	2.91	2.95	2.95	2.99	2.91	2.95
I^{-}	2.66	2.84	2.91	2.88	2.91	2.95	2.95	2.84

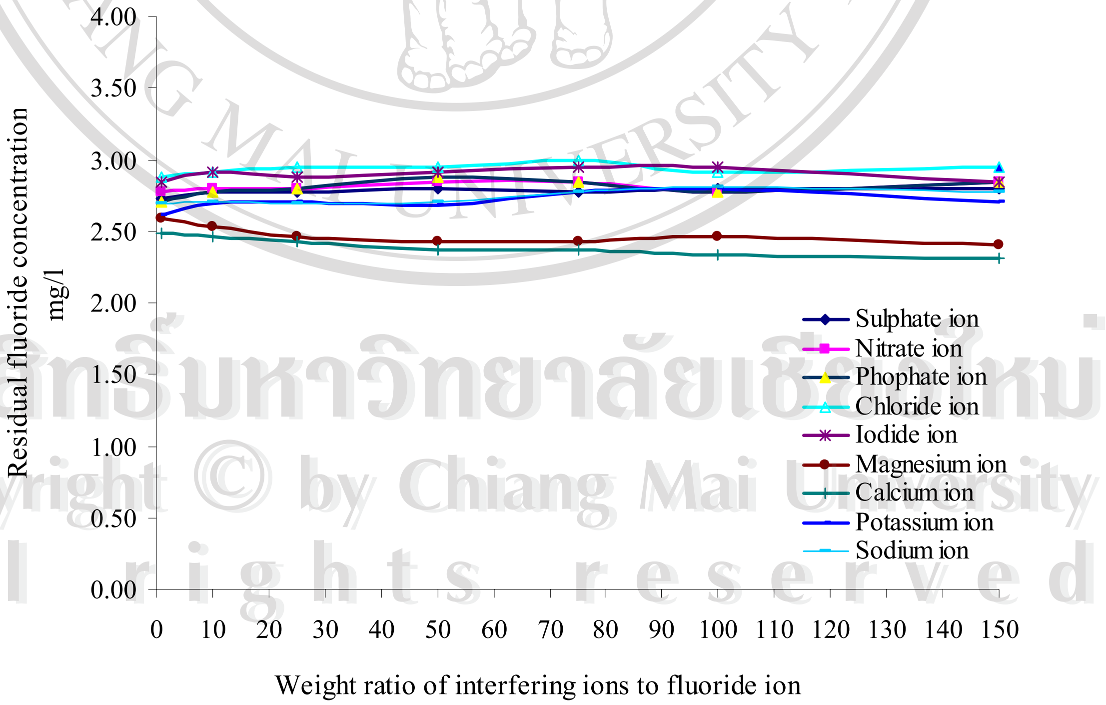

Figure 3.11 Effect of coexisting ions on the adsorption of fluoride on fired clay chips

Table 3.12 and Figure 3.11 reveal the effect of coexisting ions on fluoride adsorption by fired clay chips. It was found that the ions such as sulfate, phosphate, nitrate, chloride, iodide, sodium and potassium posed slight effect on fluoride adsorption by fired clay chips, except calcium and magnesium ions. This is probably due to the precipitate formation of CaF_2 and MgF_2, respectively. Therefore, more fluoride ions in the bulk solution tended to diminish when more amounts of calcium and magnesium ions were introduced into the fluoride solution.

3.4 Column operation for fluoride adsorption

Column operation is essential for defluoridation at household level. The objectives of the column experiment are to study the effect of primary process parameters such as the amount of adsorbent and the flow rate. The experimental set-up consisted of a glass column with diameter of 8 cm and 75 cm in length. The fired clay chips with the particle size of 4-20 was used in the study. The adsorbent was washed with distilled water. The glass column was plugged with cotton wool. The detailed arrangement of this set-up is shown in Figure 3.12

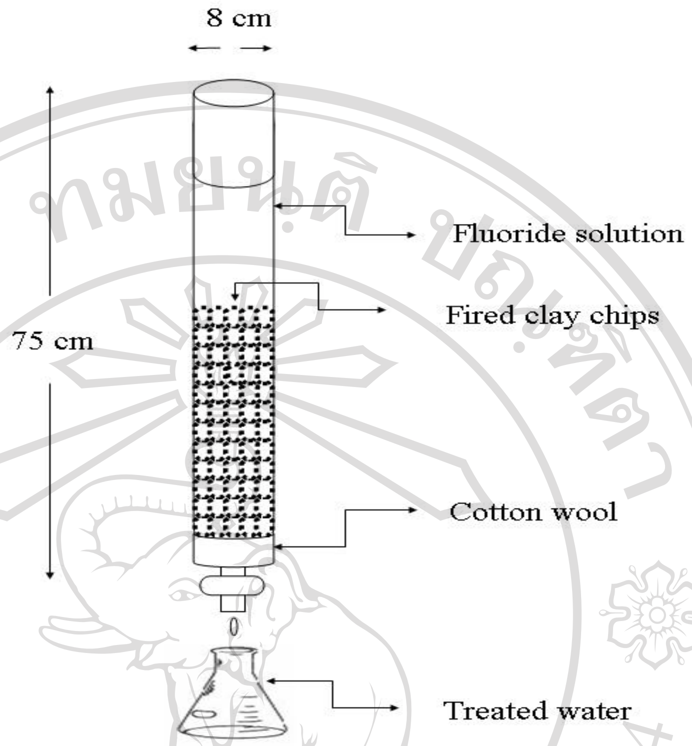

Figure 3.12 Fired clay chips defluoridator set up

3.4.1) Effect of the quantity of fired clay chips used for packing the column

To evaluate the fluoride removal efficiency of the column packed with fired clay chips, a glass column with 8 cm in diameter and 75 cm in length was packed with different amounts of adsorbing media (i.e. 500, 1000, 1500 and 2000 g). After packing the column, synthetic fluoride water with concentration of 5 mg/l was allowed to flow down the column at a flow rate of 5 ml/min. Then the column effluent was collected for fluoride analysis with the increment of 100 ml. The results pertaining to the fluoride removal efficiency of the packed column are illustrated in Table 3.13 and Figure 3.13

Table 3.13 Residual concentration of fluoride in the effluents of a packed column for defluoridation remaining after passing through the column packed with fired clay chips

Effluent volume, ml	Residual fluoride concentration, mg/l			
	500 g	1000 g	1500 g	2000 g
100	2.18	1.66	1.38	1.15
200	2.29	1.74	1.51	1.26
300	2.39	1.82	1.58	1.38
400	2.88	1.91	1.66	1.44
500	3.62	1.91	1.74	1.44
600	4.15	1.91	1.74	1.51
700	4.55	1.99	1.74	1.51
800	4.76	2.39	1.82	1.51
900	4.76	2.88	1.82	1.51
1000	4.76	3.45	1.90	1.51
1100	4.76	3.96	2.09	1.51
1200	4.76	4.34	2.51	1.66
1300	4.76	4.76	3.01	1.74
1400	-	4.76	3.45	1.82
1500	-	4.76	4.15	1.90
1600	-	4.76	4.55	2.29
1700	-	-	4.76	2.62
1800	-	-	4.76	2.88
1900	-	-	4.76	3.15
2000	-	-	4.76	3.30
2100	-	-	4.76	3.79
2200	-	-	-	4.15
2300	-	-	-	4.76
2400	-	-	-	4.76
2500	-	-	-	4.76

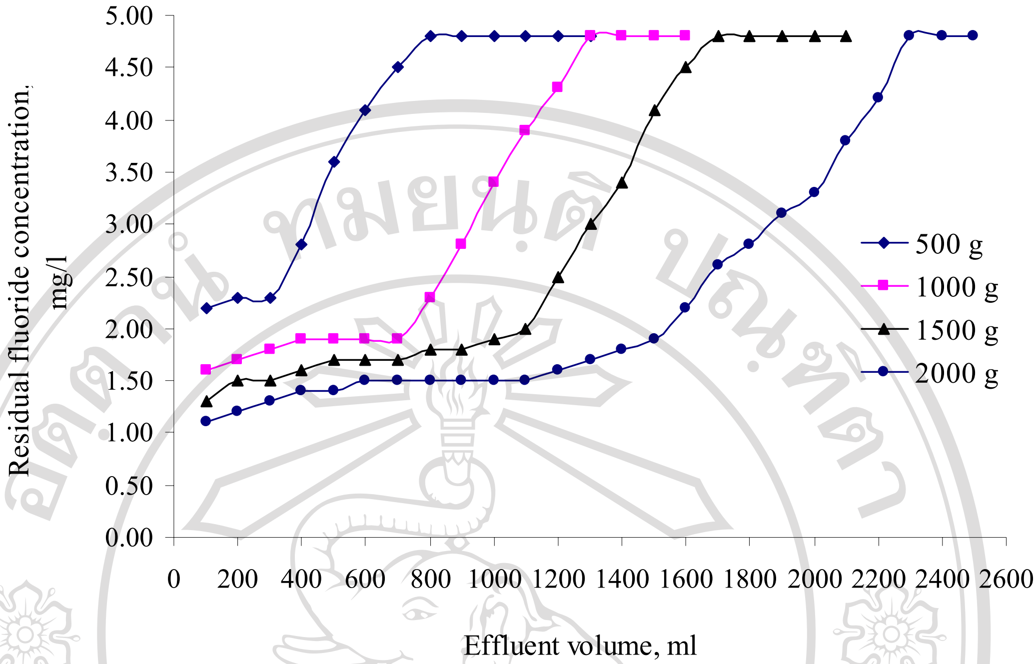

Figure 3.13 Residual fluoride concentration in the effluents of a column packed with different weights of fired clay chips

Table 3.13 and Figure 3.13 shown how the amounts of fired clay chips affect the fluoride removal efficiency. It can be seen that the quantity of fluoride removed increases with the increasing amount of fired clay chips. This is quite obvious due to the fact that at higher amount of adsorbent, more surface area and pore volume distribution are available for the adsorption. The column with 2000 g of fired clay chips provided the highest efficiency for defluoridation. It could reduce the 5 mg/l of fluoride solution to less than 1.5 mg/l in the sample volume of 500 ml. For the column with larger amount of fired clay chips, its trend in fluoride removal was expected to be more effective.

Considering the efficiency for defluoridation of the column packed with fired clay chips by different quantities, it was found that it offerred quite a low efficiency. This may be due to the capacity of fired clay chips in removing fluoride is not high (0.95 μmol/g).

3.4.2) Effect of the flow rate

The effect of flow rate on column performance for fluoride adsorption on fired clay chips were investigated in a packed column. In the second stage of removal study in the packed column, the flow rates of 5, 10 and 15 ml/min were used while the inlet fluoride concentration in each experiment was held constant at 5 mg/l and the adsorbent amount of 2000 g was used. Sampling of the fraction was performed at the increment of 100 ml and the volume collected was up to 2,000 ml. The results are shown in Table 3.14 and Figure 3.14

Table 3.14 Effect of the flow rate on column operation

Effluent volume, ml	Residual fluoride concentration, mg/l		
	Flow rate of 5 ml/min	**Flow rate of 10 ml/min**	**Flow rate of 15 ml/min**
100	1.21	1.30	1.41
200	1.26	1.32	1.45
300	1.38	1.51	1.66
400	1.44	1.66	1.82
500	1.44	1.74	1.90
600	1.51	1.74	1.90
700	1.51	1.82	1.99
800	1.51	1.82	1.99
900	1.51	1.82	1.99

Table 3.14 (continued)

Effluent volume, ml	Residual fluoride concentration, mg/l		
	Flow rate of 5 ml/min	**Flow rate of 10 ml/min**	**Flow rate of 15 ml/min**
1000	1.51	1.90	1.99
1100	1.51	1.90	2.09
1200	1.66	1.99	2.18
1300	1.74	2.09	2.39
1400	1.82	2.09	2.52
1500	1.90	2.18	2.75
1600	2.29	2.51	2.88
1700	2.62	2.75	3.05
1800	2.88	3.01	3.15
1900	3.15	3.30	3.45
2000	3.30	3.45	3.62

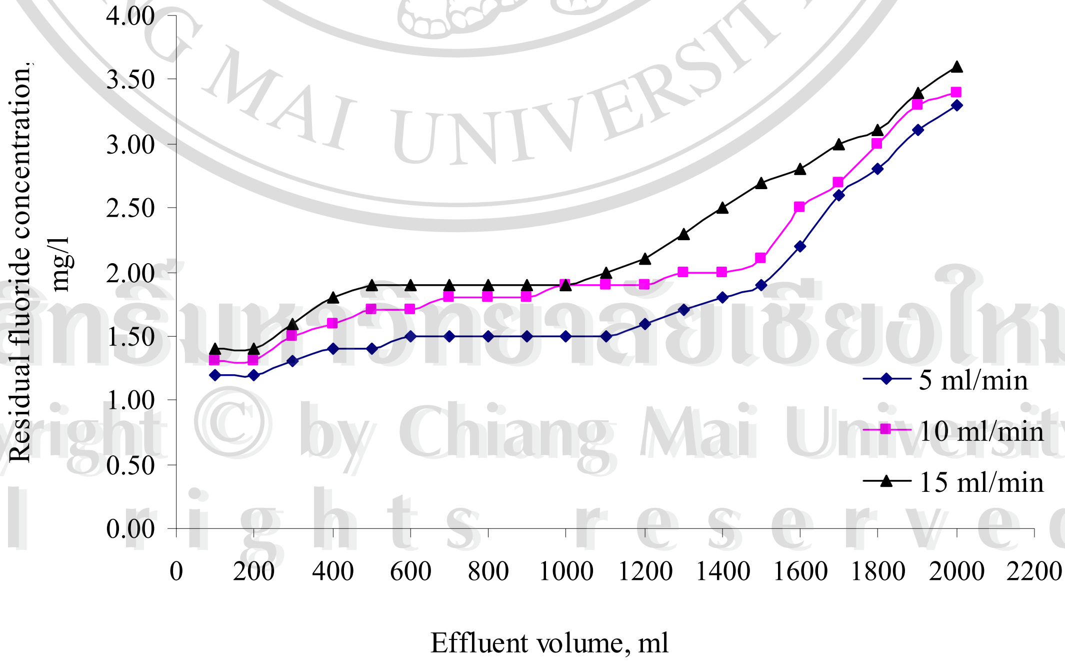

Figure 3.14 Effect of the flow rate on column operation

From Table 3.14 and Figure 3.14 it was found that fluoride adsorbed by fired clay chips in a packed column obviously depended on the flow rate. As expected, a slower flow rate produced a better removal efficiency comparing to the higher one. This is surely due to a longer contact time between fluoride ions and fired clay chips for the slower flow rate which allows the adsorption to occur at a higher extent. With the flow rate of 5 ml/min, fluoride content in water could be reduced from 5 mg/l to below 1.5 mg/l yielding 500 ml of defluoridated water. Other higher flow rates obviously demonstrated lower efficiency due to the less contact time.

However, another emerging effect occurred with column operation is the appearance of red color in the first effluent which is expected to arise from the fine dusty particles of the fired clay which adhere to the chip during the grinding process. Since the fired clay chips were used right after grinding, therefore the adhering dust would come off with the water passed through the column. Thus, in this work the method of removing the red dusty particle were designed as the following:

1) The washing step: The fired clay chips were washed with distilled water as usual manner, then filled it to a glass column and rinsed with distilled water. The rinsed water was collected at a 5 ml/min flow rate and analyzed its turbidity by a turbidimeter.

2) The further dust removal refinement with sand: The fine and coarse sand at different weights were loaded to the bottom of the column and covered it with a pad of cotton wool.. Then, passed distilled water through packed column and sampled the fraction at the increment of 100 ml using a flow rate of 5 ml/min. The fraction were analyzed for its turbidity.

The results are illustrated in Table 3.15 and Figure 3.15

Comments:

Condition 1: washing in a strainer with distillated water

Condition 2: washing in a strainer with distillated water + 300 g of coarse sand in the filtering bed

Condition 3: washing in a strainer with distillated water + 500 g of coarse sand in the filtering bed

Condition 4: washing in a strainer with distillated water + 300 g of fine sand in the filtering bed

Condition 5: washing in a strainer with distillated water + 500 g of fine sand in the filtering bed

Table 3.15 Turbidity of the washing water at various conditions

Effluent volume, ml	Turbidity, NTU				
	Condition 1	Condition 2	Condition 3	Condition 4	Condition 5
100	751	106	96.2	85.3	65.1
200	223	95.3	87.9	74.6	52.9
300	134	89.5	75.1	63.8	41.5
400	81.1	72.6	63.2	51.1	32.3
500	29.0	51.9	54.1	39.6	23.5
600	22.5	32.8	41.2	26.3	19.8
700	17.7	26.1	29.8	19.1	15.3
800	12.1	16.7	18.3	12.5	11.6
900	10.7	13.5	15.4	10.9	10.2
1000	9.20	11.2	13.7	8.98	9.01
1100	8.03	9.12	9.25	7.56	8.22
1200	6.31	7.53	8.02	6.32	7.09

Table 3.15 (continued)

Effluent volume, ml	Turbidity, NTU				
	Condition 1	Condition 2	Condition 3	Condition 4	Condition 5
1300	5.21	6.94	7.63	5.12	6.58
1400	4.26	5.48	6.22	4.96	5.23
1500	3.05	4.63	5.15	3.65	4.15
1600	2.81	3.01	4.08	3.02	3.95
1700	1.71	2.18	3.21	2.92	3.08
1800	1.53	1.95	2.95	2.56	2.52
1900	1.27	1.56	2.12	1.95	1.82
2000	1.04	1.32	1.92	1.56	1.63

Remark: Blank = 0.38 NTU

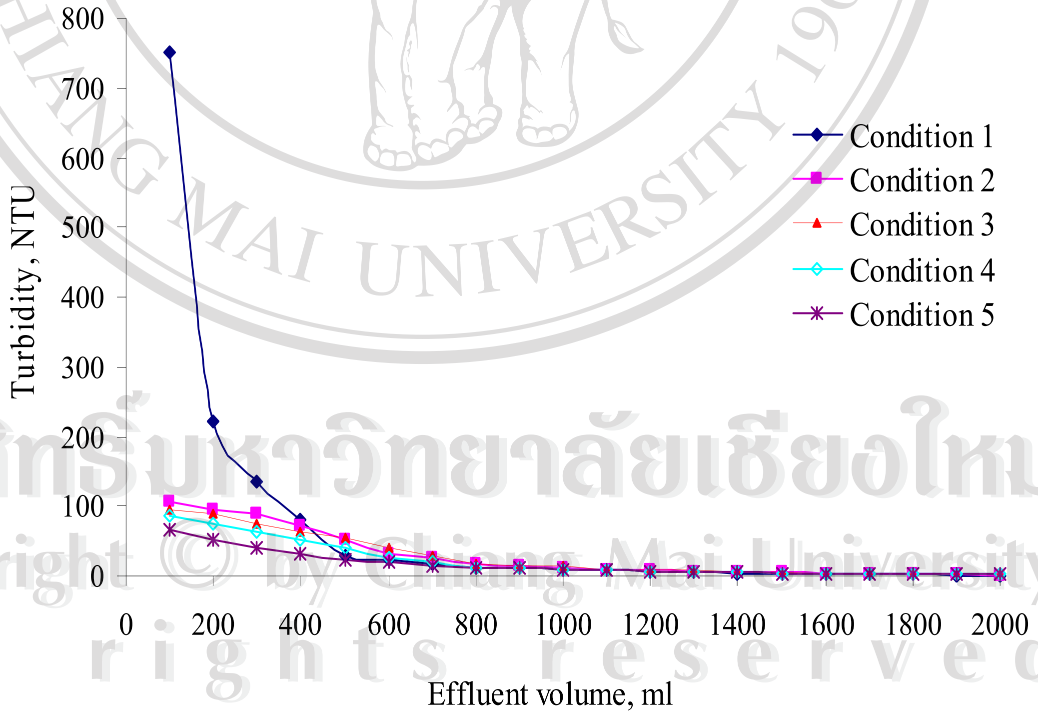

Figure 3.15 The turbidity of fired clay washing water at various conditions

From Table 3.15 and Figure 3.15, it was found that at the beginning, fine sand had more efficiency for removing the red dusty particles than the coarse sand. Increasing the weight of the fine sand also increased the removal efficiency.

The fine and coarse sand (condition 2-5) could remove the red dusty particles from the effluent. When 800 ml distilled water was passed through the column, the turbidities of the effluent are not much different no matter what the type and amount of the sand. Therefore, no necessary to use the sand for removing the red dusty particle.

In practice, approximately 1000 ml of distilled water (without sand) was used to wash the fired clay chips in the column.

3.5 Defluoridation of the potable water samples

The fluoride removal in real water samples was also demonstrated using the optimized conditions as indicated in Table 3.16. The water samples were collected form two different locations, i.e. Sai Moon School in Hang Dong district, Chiang Mai province and Ban San Kayom at Ma Khuea Chae subdistrict, Lamphun province. The informations of water samples are shown in Table 3.17

Table 3.16 The conditions for defluoridation of water sample

Item	Condition
Column dimension	8 cm i.d. x 75 cm length
Size of fired clay chips	4-20 mesh
Weight of fired clay chips	2000 g
Flow rate	5 ml/min
Temperature	Room temperature (approximately 29 °C)
pH	-
Fluoride measurements	Fluoride ion selective electrode

Table 3.17 Sample information

Sample	Fluoride concentration, mg/l	Depth, m	pH
• Ban Sai Moon School in Hang Dong district, Chiang Mai province			
Surface water in a well	4.85	10	7.45
• Ban San Kayom at Ma Khuea Chae Subdistrict , Lamphun province			
Village tap water*	6.46	-	7.51
Ground water	7.99	20	7.47

Remark: * Village tap water is produced from ground water of which its hardness, pH, chemical and odour are treated before delivering to the house.

All water samples, treated through column operation were collected and analyzed potentiometrically for every 100 ml of volume. The results of this study are presented in Table 3.18 and Figure 3.16

Table 3.18 Residual fluoride concentration in water after passing through the column of fired clay chips

Volume collected, ml	Residual fluoride concentration, mg/l		
	Ban Sai Moon School, Chiang Mai province	Ban San Kayom, Lamphun province	
	Surface water in a well (sample 1)	Ground water (sample 2)	Village tap water (sample 3)
100	1.08	1.52	1.18
200	1.13	1.88	1.40
300	1.23	2.05	1.52
400	1.23	2.14	1.73
500	1.28	2.23	1.88
600	1.28	2.33	1.97
700	1.34	2.76	2.14
800	1.40	2.88	2.33
900	1.46	3.01	2.76
1000	1.52	3.27	2.76
1100	1.73	3.27	2.88
1200	1.81	3.27	2.88
1300	1.88	3.42	3.01
1400	1.97	3.57	3.14
1500	2.05	3.72	3.27
1600	2.23	3.88	3.42
1700	2.54	4.05	3.57
1800	2.76	4.23	3.72
1900	3.01	4.60	4.05
2000	3.14	4.88	4.23

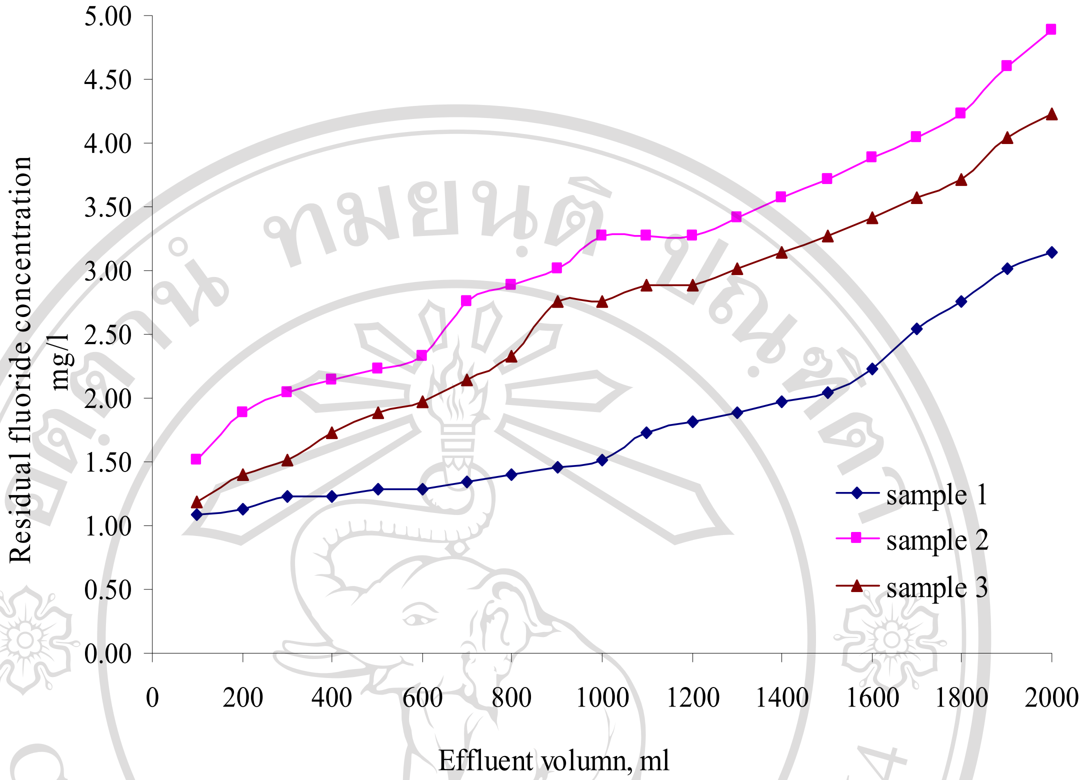

Figure 3.16 Residual fluoride concentration in water sample

From Table 3.18 and Figure 3.16, it is evidently clear that the packed column of fired clay chips is able to reduce fluoride in real water sample. This indicates that the fired clay chips is feasible to be used as the medium for removing fluoride from water. However, its efficiency on the defluoridation is less than the column packed with the fired brick chips. Their capacities, the chips of fired brick and fired clay of the same mesh size are 3.60 and 0.95 μmol/g, respectively. The lower capacity of the fired clay chips is owed to the denseness of the particle. Its denser particle causes a lower porosity which finally resulted in a lower surface area and pore volume distribution.

3.6 Water quality before and after defluoridation by fired clay chips packed column

Owing to the fact that water with standard quality is needed for consumption, therefore the water quality after defluoridation by the fired clay chips is needed to be studied. In this case, the data analysis of water quality after defluoridation were compared with the parameters of the international standard for drinking water. The tap water sample collected from Ban San Kayom was treated columnwise and the first 200 ml of effluent was analyzed for the parameters of the international standard. The result of the experiment is shown in Table 3.19

Table 3.19 Data for water quality analysis before and after defluoridation by fired clay chips

Conditions	Values	
	Before treating	**After treating**
1. Fluoride concentration, mg/l	6.46	1.18
2. Total hardness, mg/l as $CaCO_3$	69.7	73.1
3. Turbidity, NTU	0.37	0.37
4.Conductivity, μS/cm	356	388
5. pH	7.51	7.68
6. Taste	-	Acceptable
7. Odour	-	Acceptable
8. Calcium ion, mg/l as Ca	16.3	16.8
9. Magnesium ion, mg/l as Mg	7.28	7.84
10. Sulfate ion, mg/l	79.9	78.1

Table 3.19 shows the analyzed parameters of the international standard of water quality analysis before and after defluoridation by fired clay chips such as pH, hardness, turbidity, conductivity, taste, odour, fluoride, magnesium, calcium and sulfate. It is evidently clear that the parameters of water quality after defluoridation is not different from untreated water except the reduction of fluoride. Considering the data from International Standard for Drinking Water (Appendix 2), the quality of water after defluoridation by fired clay chips is found to be acceptable for human consumption and not different from standard drinking water.