CHAPTER 2

EXPERIMENTAL

The potential for defluoridation by fired clay was investigated by setting up the suitable procedures for study. Starting with lists of chemical and materials used, followed by the apparatus.

2.1 Chemicals, materials and apparatus

2.1.1 Chemicals and materials

1) Ammonium acetate, CH_3COONH_4, Puriss, Fluka, Switzerland
2) Ammonium oxalate, $(NH_4)_2C_2O_4$, A.R., BDH, England
3) Ammonia Solution, NH_3, 25%, A.R., BDH, England
4) Barium chloride dihydrate , $BaCl_2.2H_2O$, A.R., BDH, England
5) Calcium carbonate, $CaCO_3$, A.R., BDH, England
6) Calcium chloride dihydrate, $CaCl_2.2H_2O$, Puriss, Fluka, Switzerland
7) Disodium dihydrogen ethylenediamine tetraacetate dihydrate, $C_{10}H_{14}N_2Na_2O_8.2H_2O$, Prolabo produits pour lab., France
8) Ethanol, C_2H_5OH, 99%, Merck, Germany
9) Fired clay, from San Kamphang, Chiang Mai, Thailand
10) Glacial acetic acid, CH_3COOH, 99.8%, RPE, Carlo Erba, Italy
11) Magnesium chloride, $MgCl_2$, Puriss, Fluka, Switzerland
12) Potassium chloride, KCl, A.R., BDH, England

13) Sodium chloride, NaCl, RPE, Carlo Erba, Italy
14) Sodium fluoride, NaF, Pure, Merck, Germany
15) Sodium hydroxide, NaOH, A.R., Labscan, Ireland
16) Sodium iodide, NaI, A.R., BDH, England
17) Sodium nitrate, $NaNO_3$, A.R., BDH, England
18) Sodium phosphate, $Na_3PO_4.12\ H_2O$, A.R., BDH, England
19) Sodium sulfate, Na_2SO_4, A.R. Carlo Erba, Italy
20) Sulfuric acid, H_2SO_4, RPE, Carlo Erba, Italy
21) Tran-1,2 diaminocyclohexane-N,N,N',N'–tetraacetic acid (CDTA), $C_{14}H_{22}N_2O_8$, A.R., Fluka, Switzerland

2.1.2 Apparatus

1) Analytical balance, Precisa 40 SM 200A balance, Zurich, Switzerland
2) Conductometer-pH meter, Cole-Parmer, Model 5800-05, USA
3) Fluoride combination electrode, Cole-Parmer, Model 800-323-4340, USA
4) Incubator shaker, GALLENKAMP, Serial No. 8060131, UK
5) Jaw crusher machine, Japan
6) Magnetic stirrer, Cole-Parmer, model 4658, USA
7) Milli-Q water purification system, Millford, Massachusetts, USA
8) pH meter, Cole-Parmer, Model 5986-25, USA
9) Sieve size of 1-20 mesh, Maruto testing machine MFG.Co. Ltd., Japan
10) Turbidimeter, Model 2100N, Hach, USA

2.2 Preparation of the fired clay samples, standard solutions and reagents

All solutions were prepared using deionized distilled water obtained from a Milli-Q system.

2.2.1 Preparation of the fired clay chips

Fired clay samples were obtained from a local vender in San Kamphang district, Chiang Mai province, Thailand. Before using, they were broken by hammer and crushed into chips by jaw crusher machine. Sieved to the size of 20-<1 mesh and washed with distilled water before use.

2.2.2 Preparation of the solutions

1) Acetic acid, 0.1 M

Pipetted 0.57 ml of acetic acid into a 100 ml volumetric flask and diluted to the volume with deionized distilled water.

2) Ammonium hydroxide, 1 M

15.10 ml of 25% NH_3 was diluted with deionized distilled water to 200 ml in a volumetric flask.

3) Sodium hydroxide, 6 M and 0.1 M

Prepared 1000 ml of 6 M sodium hydroxide by weighing 240 g of NaOH, dissolved and made up the volume with deionized distilled water.

0.1 M NaOH was prepared by diluting 6 M NaOH to 500 ml with deionized distilled water

4) Stock standard fluoride solution

Fluoride solution was prepared by using NaF. An accurate weight of 2.21 g NaF was dissolved with deionized distilled water and diluted to 1000 ml in a volumetric flask to give a stock solution of 1000 mg/l F^-. For the fluoride solution with concentration range from 1-500 mg/l, they were prepared by diluting appropriate volumes of 1000 mg/l stock solution with deionized distilled water.

5) Stock solution of interfering ions (calcium, chloride, iodide, magnesium, nitrate, phosphate, potassium, sodium and sulfate solution), 1000 mg/l

1000 mg/l solutions of interfering ions (Ca^{2+}, Cl^-, I^-, Mg^{2+}, NO_3^-, $PO^{3-}{}_4$, K^+, Na^+ and $SO^{2-}{}_4$) were prepared by the compounds as indicated in Table 2.1. Weighing the compound with appropriate weight accurately, dissolved and filled into 1 liter of volumetric flask with deionized distilled water.

Table 2.1 Preparation of solutions with interfering ions

No.	Stock Solution of	Compound Used	Weight, g
1	Ca^{2+}	$CaCl_2.2H_2O$	3.67
2	Cl^-	NaCl	1.65
3	I^-	NaI	1.18
4	Mg^{2+}	$MgCl_2.6H_2O$	8.36
5	NO_3^-	$NaNO_3$	1.37
6	PO_4^{3-}	$Na_3PO_4.12H_2O$	4.00
7	K^+	KCl	1.90
8	Na^+	NaCl	2.54
9	SO_4^{2-}	Na_2SO_4	1.48

6) Mixture of fluoride ion and interfering ions at the weight ratio of 1:1 to 1:150

Pipetted 100 mg/l of fluoride solution and 1000 mg/l of interfering ion (Ca^{2+}, Mg^{2+}, K^+, Na^+, SO^{2-}_4, PO^{3-}_4, NO^-_3, Cl^- and I^-) solutions with appropriate volumes as indicated in Table 2.2, and diluted to the volume in a 100 ml volumetric flask.

Table 2.2 Preparation of mixed solution of fluoride and interfering ions

Ratio of fluoride ion: Interfering ions	Volume of 100 mg/l fluoride solution, ml	Volume of 1000 mg/l interfering ions, ml
1:1	5.00	0.50
1:10	5.00	5.00
1:25	5.00	12.50
1:50	5.00	25.00
1:75	5.00	37.50
1:100	5.00	50.00
1:150	5.00	75.00

7) Total Ionic Strength Adjustment Buffer; TISAB solution

A 500 ml of distilled water was added into 1000 ml beaker. Placed the beaker on a magnetic stirrer. 58 g of NaCl, 57 ml of CH_3COOH and 4.0 g of CDTA were dissolved. After the solid dissolved, the solution was cooled and adjusted the pH to 5-5.5 with 6 M NaOH. The solution was cooled down further to the room temperature (approximately 29 °C), transferred it to a 1000 ml volumetric flask and diluted to the volume with distilled water.

2.3 Procedures

2.3.1 Characteristics of the fired clay chips

a) Determination of the chemical compositions of fired clay

Clay contains many inorganic substances such as SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O and K_2O. The main compositions of clay such as SiO_2, Al_2O_3 and Fe_2O_3 were analyzed by gravimetric method. At the same time, trace components in the clay such as TiO_2, CaO, MgO, Na_2O and K_2O were analyzed instrumentally by the technique of atomic absorption spectrophotometry and UV-Visible spectrometry. (Chemical compositions of fired clay were analyzed by office of Mineral Resource Region III(Chiang Mai), Chiang Mai, Thailand)

b) Determination of surface area, pore volume distribution and average pore radius

The fired clay chips with the size of 4-20 mesh was used for the determination of surface area, pore volume distribution and average pore radius. They were determined by five-point BET method using a Autosorb 1, gas sorption system. The P/P_0 ratios were 0.0983, 0.1602, 0.2106, 0.2604 and 0.3102. A gaseous mixture of nitrogen and helium combined using a gas mixture was allowed to flow through the system at a constant rate of 30 ml/min. The nitrogen gas sample was injected with a one milliliter syringe to calibrate the analyzer for each gas composition. The fired clay chips sample was dried at 473 K and degassed in the sample holder for 1 hour. The adsorption surface area and desorption surface area of fired clay chips was measured. The surface area of the fired clay chips was calculated based on the desorption surface area and the dried weight of the sample after analysis. (Surface area, pore volume distribution and average pore radius were analyzed by

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

Prepared 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l standard fluoride solutions by serial dilution of 100 mg/l stock standard fluoride solution. Pipetted 10 ml of each standard fluoride into the 50 ml beaker containing 10 ml TISAB solution. After the solution was mixed well, measured the potential of the fluoride solution by fluoride ion selective electrode. The electrode was allowed to be equilibrated for 3 minutes before reading the potential. Constructed the calibration curve by plotting the voltage of each fluoride concentration against the corresponding logarithm of concentration.

2.3.3 Batch experiment for fluoride adsorption onto fired clay chips

Batch adsorption tests were conducted to investigate the effect of various parameters on fluoride adsorption efficiency onto fired clay chips such as the effect of particle size of fired clay, static and dynamic conditions, agitation rate, contact time, initial fluoride concentration, pH, temperature and coexisting ions.

a) Effect of the particle size of fired clay chips

This study was to investigate the influence of the particle size of fired clay chips having the mesh-size of 4-20, 1-4 and <1 mesh that provided the highest efficiency for defluoridation. These crushed and sieved fired clay chips will be used throughout the experiment. Weighed accurately 20.00 g of fired clay chips in a 250 ml Erlenmeyer flask and added 30 ml of 5 mg/l fluoride solution into the flask. The suspension was shaken at room temperature for 3 hours at 150 rpm. The supernatant was filtered through Whatman No.1 to remove suspended fired clay. A 10.00 ml of supernatant was taken into a 50 ml beaker and mixed with 10.00 ml TISAB solution and stirred with a magnetic bar. The potential of the solution mixture was measured by fluoride ion selective electrode. The blank solution without fluoride ion was prepared as the same condition.

b) Effect of the static and dynamic conditions

A 20.00 g of fired clay chips was weighed into a flask containing 30 ml of 5.0 mg/l fluoride solution. The efficiency of fluoride adsorption onto fired clay chips were evaluated under static and dynamic conditions.

Under the dynamic condition, the mixture was shaken by shaker machine at 150 rpm for a certain time interval of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hours. The supernatant was filtered before assaying the fluoride concentration. Pipetted 10 ml of the filtrate, then mixed well with TISAB solution in the beaker. The residual fluoride which remained in the solution was determined by fluoride ion selective electrode.

As for the static condition, the mixture was left undisturbed for the certain time interval of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hours in room temperature. The residual fluoride concentration was determined by treating exactly the same way as in the dynamic condition.

c) Effect of the agitation rate

A 20.00 g of fired clay chips was accurately weighed into a 250 ml Erlenmeyer flask. Added 30 ml of 5 mg/l fluoride solution into the flask and shook by shaker machine at different agitation rates from 50, 100, 150, 200, 250, 300, 400 and 500 rpm. These mixtures were shaken for three hours equilibrating time at room temperature. The supernatant was filtered through Whatman No.1. The residual fluoride remained in the filtrate was determined potentiometrically as described above.

d) Effects of the contact time and initial fluoride concentration

Weighed accurately 20.00 g of fired clay chips into a 250 ml Erlenmeyer flask which contained different concentrations of fluoride solution at 5, 10 and 20 mg/l. The mixture was stirred at 150 rpm at different time intervals ranging from 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 hours. The residual fluoride concentration of each batch equilibrated was determined by F^--ISE.

e) Effect of the pH

A 30 ml each of 5, 10, 20 and 30 mg/l fluoride solution at different pH ranging from 3, 4, 5, 6, 7, 8, and 9 were added into a 250 ml of Erlenmeyer flask. Weighed accurately 20.00 g of fired clay chips and added in the solution. The suspension were shaken at 150 rpm for 2.0 hours. The fluoride remained in solution was analyzed potentiometrically.

f) Effect of the temperature

Weighed 20.00 g of fired clay chips into a 250 ml Erlenmeyer flask containing 30 ml of fluoride solution with concentration ranges from 5 to 300 mg/l. The adsorbent and fluoride solution in each flask were shaken for 2.0 hours at 30, 40 and 50 °C, respectively. Then the fluoride concentration was determined in the same manner.

g) Effect of the coexisting ions

A 20.00 g of fired clay chips was weighed into a flask containing 30 ml of the fluoride solution. The solution mixture consisted of fluoride and interfering ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, $SO^{2-}{}_4$, $PO^{3-}{}_4$, $NO^-{}_3$, Cl^- and I^-) at different weight ratios of 1:1, 1:10, 1:25, 1:50, 1:75, 1:100 and 1:150. The solution-fired clay chips system was then equilibrated in the usual manner and the residual fluoride remained in the solution was determined by F^--ISE.

2.3.4 Column experiment for fluoride adsorption on fired clay chips

To evaluate the fluoride adsorption performance of the fired clay chips in a flow-through system, the column experiments were investigated to study the effect of the amount of fired clay chips and the effect of the flow rate on column operation.

In the preparation step of the column experiment, the glass column with 8 cm i.d. and 75 cm length was used for a study. The ends of the glass column was plugged by cotton pad before filling the adsorbent to prevent the clogging of the stopcock passage and the fired clay chip (4-20 mesh) was washed with distilled water before use.

a) Effect of the amount of fired clay chips

Weighed the fired clay chips by the amount of 500, 1000, 1500 and 2000 g, one at a time into a glass column and fed 5.0 mg/l fluoride solution to the column. Samples of the effluent were periodically collected and analyzed potentiometrically at the increment of 100 ml and the flow rate of 5 ml/min.

b) Effect of the flow rate

To conduct this experiment, weighed 2000 g of fired clay chips and packed into the column. The 5.0 mg/l fluoride concentration was allowed to flow down the column at different flow rates of 5, 10 and 15 ml/min. The effluent was collected at the increment of 100 ml and analyzed for the residual fluoride.

2.3.5 Defluoridation of the potable water samples

Water samples were collected from Saimoon School in Hang Dong District, Chiang Mai province and San Kayom Village at Ma Khuea Chae Subdistrict, in Lamphun province, North of Thailand. These water samples had fluoride level more than 1.5 mg/l. The samples were treated in the column and operated as the following conditions listed in Table 2.3.

Table 2.3 The column characteristics and its condition for defluoridation of water sample

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

The sample fraction was collected at the increment of 100 ml until a total of 2000 ml was obtained and determined the amount of fluoride potentiometrically.

2.3.6 Investigation of the water quality before and after defluoridation by fired clay chips column

To evaluate the water quality before and after treating by using fired clay chips as adsorbent. This study focuses on analyzing the quality of water by using different physical and chemical parameters such as conductivity, turbidity, taste, odour, total hardness, pH, fluoride, calcium, magnesium and sulfate. The water sample was collected from the column experiment as the fluoride concentration is less than 1.5 mg/l. The procedures used in water quality analysis are shown below:

1) Conductivity: The conductivity of water was measured by a conductometer-pH meter.

2) pH: This parameter was also measured by a pH meter. Each time before use, the pH electrode was calibrated with buffer pH 4 and 10 solutions.

3) Turbidity: The turbidity of water samples was measured by a turbidimeter.

4) Taste and odour: Taste and odour were actually tested.

5) Temperature: The water temperature was measured by a thermometer.

6) Total hardness as $CaCO_3$: 25 ml aliquot of water sample was pipetted into a 250 ml Erlenmeyer flask. Added 10 ml of buffer pH 10 for adjusting the pH to 10 ± 0.1 and dropped Eriochrome black T as an indicator. Titrated with 0.0100 M sodium EDTA dihydrate titrant until color changing from violet to blue then recorded

the volume of sodium EDTA dihydrate and calculated the total hardness. The experiments were triplicately run.

7) Calcium (Ca^{2+}) and Magnesium (Mg^{2+}): Calcium and Magnesium ions are present in all waters and often referred to as hardness factors.

Magnesium ion was determined by pipetting 25.00 ml of water sample in a 250 ml Erlenmeyer flask. Added 5 ml of NH_4OH into the flask to control the basic condition. Boiling the solution for 2 minutes and dropped 3 M $(NH_4)_2C_2O_4$ to precipitate calcium ion as calcium oxalate. After cooling, the precipitant was taken out by filtration and washed it with distilled water. Collected the solution, added 10 ml of buffer pH 10 and dropped Eriochrome black T as an indicator. Titrated with 0.01 M EDTA titrant until color changing from violet to blue then recorded the volume of EDTA.

Calcium ion concentration was obtained by subtraction of the volumes of sodium EDTA dihydrate used for determining total hardness and magnesium ion.

8) Sulfate (SO_4^{2-}): Sulfate ion was determined by nephelometric method, pipetted 25 ml water sample into a 250 ml Erlenmeyer flask. A 5 ml of conditioning reagent was added and the solution was continuously stirred, then followed by adding 5 ml of 5 M barium chloride and stirring continued for one minute. Immediately afterwards, the solution was transferred to a cuvette and the adsorption at 420 nm was measured repeatedly over a period of 2 to 3 minutes. The standard sulfate ion was treated in exactly the same way as the sample.

As for the condition reagents; it was prepared by mixing 15 ml of conc. hydrochloric acid, 150 ml of water, 50 ml of ethanol and 35.5 g of sodium chloride into 500 ml beaker. Then, 25 ml of glycerine was added and mixed well the solution.