FLUORIDE REMOVAL BY ADSORPTION USING OIL PALM WASTE

By

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Thesis submitted to

UNIVERSITI SAINS MALAYSIA

To fulfill the requirement of graduation

BACHELOR DEGREE IN CIVIL ENGINEERING

School of Civil Engineering,
Universiti Sains Malaysia

April 2005

ACKNOWLEDGEMENT

First of all I would like to say my heartiest thanks to Allah for giving me strength and spirit to accomplish my task (Final Year Project) successfully. I would like to take this opportunity to give my very special thanks to my supervisor Dr. Mohamed Hasnain Isa, with all his supervisions and guidance; I have been able to understand more about managing and conducting an excellent thesis. I would also like to thank my parent and all my friends especially to Mr. Mohd. Izziudin Abd. Malik, Mr. Ragunathan, Ms. Norshafa, Ms. Afiza Amran and Ms. Naimah Ibrahim for their contributions, ideas and helps, while my task in progress. I am really motivated and encouraged to do well in the project. I am also not to forget, to say thanks to all the technicians especially Puan Nurul that have been very supportive and tolerate. Finally I would like to acknowledge School of Civil and School of Material for all the helps and encouragement given to all final year students. I am grateful to School of Civil and material for providing conductive working environment.

ABSTRAK

Florida wujud di dalam kandungan air secara umumnya, sama ada dalam bekalan air atau air kumbahan. Florida tidak akan memberi kesan buruk kepada manusia dan hidupan lain sehingga kepada satu amaun tertentu sahaja dan untuk amaun yang lebih besar atau lebih tinggi daripada1.0 mg/l, florida bukan lagi sebagai satu keperluan. Daripada sesetangah kajian yang dijalankan, didapati had keperluan florida bagi manusia dan haiwan adalah sangat rendah. Oleh kerana itu, keperluan terhadap kajian dalam mencari bahan penjerap terbaik sebagai ejen penyingkiran kandungan florida yang tinggi adalah penting. Kebanyakan kajian – kajian terdahulu menunjukkan bahawa penjerapan merupakan kaedah yang terbaik untuk menyingkirkan florida sehingga 95% keberkesanannya dan didapati penjerapan pengelompokan adalah cara yang digemari untuk digunakan. Projek ini mengetengahkan produk – produk hasil buangan kelapa sawit seperti sabut, habuk, tempurung dan abu sebagai bahan yang sesuai dan berpotensi, malah menjimatkan bagi tujuan penyingkiran florida. Projek ini juga menggunakan penjerapan berkelompok dan kesemua bahan penjerap telah dirawat menggunakan asid. Kajian ini mendapati, abu adalah bahan penjerap yang paling berkesan bagi menyingkirkan florida pada pH 2 dan ujikaji ini telah dijalankan selama 240 minit masa kisaran. Tiga model utama yang sesuai dengan penjanaan isoterma adalah model Freundlich, model BET dan model Langmuir. Kajian ini mendapati bahawa Isoterma Langmuir mematuhi penjerapan florida dengan berkesan dan model Langmuir dipilih kerana nilai R^2 yang tertinggi sekali. Kecekapan penyingkiran yang dicapai oleh abu adalah dalam 92.5 %.

ABSTRACT

Fluoride is commonly found in water and wastewater. Fluoride would not cause any bad impact to human and other life nature, up to certain amount only and for some higher amount or more than 1.0 mg/l, fluoride is no more as a requirement. From some studies, the permissible limits of fluoride for both humans and animals requirement was found to be very low. Therefore, the needs of studies to search for the best adsorbent, as an agent to remove high amount of fluoride is important. Most of the previous studies shown that adsorption is the best way to remove fluoride almost up to 95 % effectiveness and found that batch adsorption seems to be the favourite method to be used. This project is highlighted on oil palm waste such as fibre, sawdust, shell and ash as suitable and potential, yet economical materials for the purpose of fluoride removal. This project also used batch adsorption and all adsorbent were treated with acid. This study found that ash is the most effective adsorbent to remove fluoride at pH 2 and the experiment were carried out for about 240 minutes agitation time. Three main models suits with the isotherms generation are Freundlich model, BET model and Langmuir model. The present study found that Langmuir Isotherm followed the Fluoride adsorption effectively and the Langmuir was chosen due to the highest value of R^2. The efficiency of removal achieved by ash as the adsorbent is about 92.5 %.

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1 - INTRODUCTION

Fluoride is a substance that is present in some wastewaters. Fluoride is present naturally in the earth's crust or is discharged from agricultural and industrial activities such as steel, aluminum, glass and electroplating.

Animals and humans need fluoride in their daily life but the amount must be within the permissible limit of 0.5 – 1.0 mg/L. Those amounts are beneficial for the production and maintenance of healthy bones and teeth. Higher intake of fluoride could cause dental and skeletal fluorosis and ossification of tendon and ligaments [Hichour et al., 2000]. .Discharging of wastewater containing high contents of fluoride would increase the contamination of groundwater. There are many people facing skeletal and dental fluorosis in the world especially in China, India, Pakistan and Thailand [Reardon and Wang, 2000]. Many groundwater sources contain higher fluoride content than the maximum permissible amount of 1.5 mg/L. In China, it was reported as high as 5 mg/L in Cang Zou City [Liu et al., 1983]. Therefore a strict regulation of environment emerged. On the other hand, the US EPA established a standard of 4 mg/L of fluoride only for the discharge from wastewater treatment plants.

This study concentrates on investigating the fluoride adsorption behaviour of low cost materials viz., oil palm fibre and oil palm shell. The present research studies the beneficial use of oil palm wastes acting as a cheap pollution control material.

1.1) Objective

1.1.1) List of main objectives

a) Search for an economical way to reduce the amount of fluoride in water.

b) Contribute more information for future studies to enhance the adsorption technology for the betterment of human kind.

1.1.2) Research objectives

a) To study the use of oil palm by – products as an adsorbent for fluoride removal.

b) To determine the optimum conditions (pH, agitation time) of the process.

c) To highlights the potential of low cost material available from an easy source which is oil palm waste, for the use in science and technology.

d) To obtain isotherm equations for the process.

1.2) Research Scope

The study will explore the optimum adsorption conditions for fluoride removal using low cost material. The use of low cost material, in this case, oil palm waste such as sawdust, fibre and ash were the main focus of the study. Some of the adsorbents were first treated with acid in order to improve their adsorption characteristics. The study will look on the best condition for the adsorption of fluoride, in terms of pH, agitation time and the best adsorbent to be used. The mathematical relationships considered in this scope were the three models i.e. Freundlich, Langmuir and BET models. These models will present the relationship on adsorbent-adsorbate.

2 - LITERATURE REVIEW

2.1) Adsorption

Generally, adsorption can be defined as a phenomenon or a process of removal of substances from a solution (either gaseous or liquid) by using solids as an adsorbent or an agent of the removal. The process involves, simply just preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate [Slejko, 1985]. Adsorption is a process of collecting soluble substances in solution and it happens on a suitable interface, either between the liquid and a gas, a solid, or another liquid [Metcalf & Eddy, 1979]. Adsorption phenomenon happens in nature in physical, chemical, and biological systems. Adsorption process uses adsorbents such as activated carbon to remove pollutants and commonly, the process is widely used in industrial applications and in the purification of water and wastewater. Historically, the adsorption terminology was used in describing the concentrating of a component in particular, at a specific interface relative to an adjacent solution or other bulk phase. Absolute adsorption or adsorption of an individual component refers to the actual quantity of the component present during the adsorbing phase versus its own excess, relative to the bulk liquid. This was simply known as a surface concentration [Kipling, 1965].

2.2) Adsorbents

Adsorbents play a major role in the adsorption process. An adsorbent functions as an agent that determines the difference between two molecules in the mixture. It provides the required surface for the removal of contaminants. The effectiveness of an adsorbent depends mainly on its specific surface area besides the structure and the chemical properties itself. Smaller specific surface area will increase the efficiency of the adsorbent. In many researches, activated carbon has been used as adsorbent. Activated carbon is especially known for its effectiveness in removing organic, inorganic heavy metal pollutants chemical from wastewater. Adsorbents need to be dried first, before the adsorption process start, due to its capability to adsorb water vapour from the atmosphere. Usually the drying process is done by heating them for 2 hours at 110°C to 120°C. The temperature depends on the solid type or the properties of the adsorbents. This is to prevent alteration by being heated.

2.3) Factors Affecting Adsorption

2.3.1) pH

pH is an important parameter to be observed in any adsorption process. An optimum pH is one of the main objectives aimed in the adsorption process. Not all adsorption process suits with natural pH. Adsorption for fluoride removal is best at low pH [Swope and Hess, 1937].

2.3.2) Agitation time

Agitation time also needs to be considered in adsorption process. It is important to determine the best time result for the adsorption process to succeed. Too much time will make the process inefficient and not really a good practice. One of the objectives of the process is to determine the optimum agitation time. The lesser the time taken, the better. But, it is depend on the workability and the effectiveness of the adsorbents, where there are some cases that require more time, in order to see the removal effectiveness. If the process were done in batch method, it is easier to take the agitation time periodically, rather than the column method, where by using batch method, samples can be taken one by one in at definite times. Example, for each sample from a batch that consist of 10 samples, is being taken one by one according to a periodic time, like every 10 minutes. Then, each time the sample is taken, the progress of the removal process will be evaluated, whether the removal is successful or vice versa according to time.

2.3.3) Adsorbent dose

Adsorbent dose is the amount of adsorbent required for a certain solution's concentration. This parameter depends on the level of concentration of the solution. Higher amount of the adsorbent will be required when the concentration of the solution is high. Sometimes, the adsorbent dose can also be determined in terms of concentration, often used when dealing with half liquid-solid adsorbent or purely liquid adsorbent. Theoretically, a small amount of adsorbent cannot cope with a high concentration of solution.

2.4) Adsorption studies

2.4.1) Batch Equilibrium Technique

This technique is often used in measuring adsorption from liquids by solids where the liquid usually refers to wastewater, and solid refers to the adsorbent. In this method, both solid and liquid (known amounts), are mixed together and agitated by shaking. An equilibrium is established at a specified temperature and the changes of constituent composition in the liquid is determined. The number of samples depends on the required accuracy of the results required. The agitation time required varies considerably with the type of system being investigated [Kipling, 1965].

2.4.2) Fix-Bed Column Technique

Fix-bed column is often used by contacting the solutions with the adsorbent filled in the column. The wastewater will be applied from the top of the column and withdrawn at the bottom. At the bottom of the column, an underdrain is provided and the adsorbent is held within. It is necessary to apply backwash and surface wash to prevent head loss rising up. It can be operated singly, in series or in parallel. Surface clogging is the only problem that occurs due to the suspended solid. Therefore surface wash is the solution for the clogging matter.

2.4.3) Moving Bed

The moving bed or continuous, counter-current adsorption configuration is proving to have substantial advantages for certain application. In this configuration, the adsorbent is moved around a single loop of interconnected vessels such that adsorption, regeneration and backwashing are taking place simultaneously in different locations. The system is operated with adsorbent moving in one direction and all solutions in the other [Slejko, 1985].

2.5) Isotherms

2.5.1) Freundlich isotherm equation

Common equation of freundlich is stated below:

$x/m = ά . c^{1/n}$

Where x is the weight of adsorbate,

m is the weight of solid (adsorbent),

c is the concentration of the solution at equilibrium; ά and n are constants, the form 1/n being used to emphasize that *c* is raised to a power less than unity. The empirical constants, ά and n, in this equation can be evaluated by plotting x/m versus *c* (as shown in **Figure 2.1**) on double logarithmic paper.

$\text{Log}(x/m) = \text{Log}\,\acute{\alpha} + (1/n)\log c$

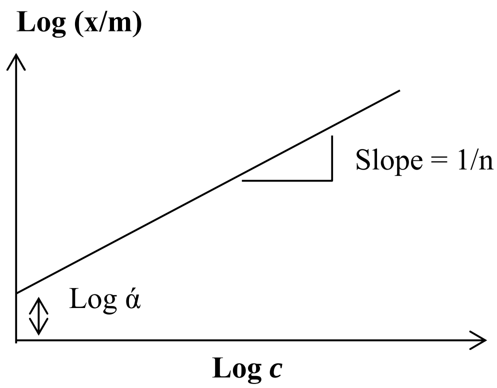

Figure 2.1: Freundlich Isotherm

Freundlich used the equation extensively even though he is not the origin. The equation is also used to describe the adsorption of gas from solid. Unfortunately the Freundlich equation is limited to adsorption from dilute solutions.

2.5.2) Langmuir isotherm equation

The Langmuir equation is:

$x/m = (\acute{\alpha}\, n\, c)/(1 + n\, c)$

Where x/m is the amount adsorbed per unit weight of adsorbent,

ά and n is the empirical constants and,

c is the equilibrium concentration of adsorbate in solution after adsorption.

The empirical constants, ά and n, in this equation can be evaluated by plotting 1/(x/m) versus 1/*c* as shown in **Figure 2.2.**

$$1/(x/m) = (1 + n \cdot c)/(\acute{\alpha} \cdot n \cdot c)$$

$$= 1/(\acute{\alpha} \cdot n \cdot c) + 1/\acute{\alpha}$$

$$= (1/\acute{\alpha} \cdot n) \times (1/c) + (1/\acute{\alpha})$$

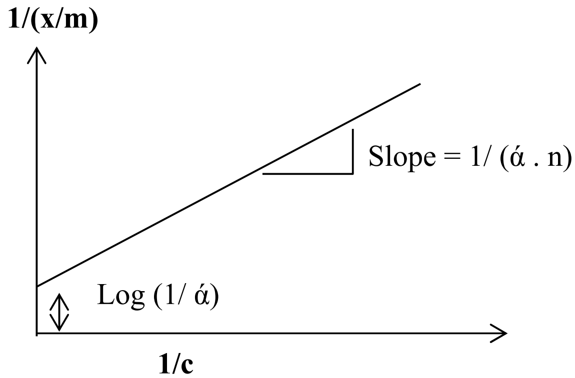

Figure 2.2: Langmuir Isotherm

The equation is derived from rational considerations, and after some enhancement from the Freundlich equation. Langmuir equation was developing by considering 2 assumptions and they are:

1) A fix number of accessible sites are available on the adsorbent surface
2) Adsorption is reversible.

Equilibrium is the stage where the rate of adsorption of molecules onto the surface is equal with rate of desorption of molecules from the surface.[Metcalff & Eddy, 1979] The difference between the amounts adsorbed at a certain concentration, and the amount that can be adsorbed at that concentration is zero when the equilibrium is reached. General Langmuir isotherm is shown in **Figure 2.3**

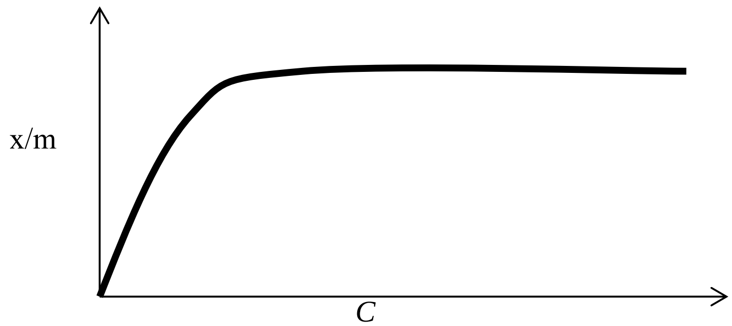

Figure 2.3: Langmuir Isotherm Theoritically

2.5.3) Brunauer-Emmet-Teller (BET) Isotherm

The Brunauer-Emmet-Teller (BET) isotherm equation is,

$$\frac{x}{m} = \frac{ACx_m}{(C_s - C)\left[1 + (A-1)\frac{C}{C_s}\right]}$$

$$\frac{C}{(C_s - C)\frac{x}{m}} = \frac{1}{Ax_m} + \frac{A-1}{Ax_m}\left[\frac{C}{C_s}\right]$$

Where C = concentration of adsorbate in solution after complete adsorption (mg/l)

C_s = saturation of concentration (mg/l)

x_m = amount of adsorbate adsorbed in forming a complete monolayer (mg/g)

A = constant

The empirical constants, A in this equation can be evaluated by plotting C/[(C_s – C)(x/m)] versus C/C_s as shown in **Figure 2.4**

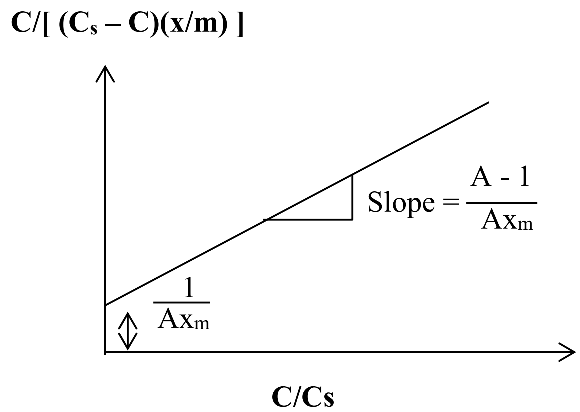

Figure 2.4: BET Isotherm

2.6) Low Cost Materials

The desire to have a low cost material is surely needed from the stand-point of economic treatment. Nowadays, there are many studies done especially on low cost materials such as peat, wood chips, hydroxyapatite, fluorspar, calcite, quartz, and quartz activated by ferric ions [Fan et al; 2003]. The main considerations for adsorption with low cost materials are cost and effectiveness. Low cost will give a big impact to the application of adsorption technology. The efficiency of adsorption depends on the adsorbent's properties. Therefore, dealing with the adsorbent materials is more important rather than looking for other parameters to focus on.

2.7) Potential and effectiveness of low cost materials

Methods for the removal unwanted soluble constituents of water include ion exchange, electrodialysis and membrane process. These techniques are effective in removing contaminants [Fan et al., 2003]. They can remove fluoride to a suitable level, but they are expensive and have operational difficulties such as frequent regeneration of membrane, cleaning of the scales and fouling. Therefore, recent attention of scientists has been devoted to the study of low cost, but really effective materials.

Studies have been done on several materials that can be considered as low cost. They are hydroxyapatite, fluorspar, calcite, quartz, and quartz activated by ferric ions [Fan et al., 2003]. Among those materials, hydroxyapatite has the highest fluoride adsorption capacity. At the initial concentrations range from 2.5 x 10^{-5} to 6.34 x 10^{-2} mg/l. Besides, hydroxyapatite can adsorb 90% of fluoride at a near natural pH of 6. On the other hand, fluorspar can remove about 25% of fluoride from the solution with the same initial concentration. Following, the next material is calcite with 17.6% of removal, activated quartz with 12% of removal [Fan et al., 2003].

Activated red mud is quite good in removing fluoride from solutions. In one study, 82% removal was reached with activated red mud [Cengeloglu et al., 2002]. The optimum pH for the adsorption was 5.5, with a contact time of 2 hours. Red mud is an unwanted product during the alkaline – leaching of bauxite in the Bayer process. The fluoride adsorption capacity of the activated form was found to be higher than that of the original form. The study found that the results followed the Langmuir isotherm equation [Cengeloglu et al., 2002].

Yan et. al, (2003) found that Aligned Carbon Nanotubes (ACNTs) gives the best removal capacity of fluoride, compared to activated carbon, even though it's specific area is much lower than activated carbon, with 687 m^2/g of activated carbon compared to ACNTs with only 0.47cm^3/g respectively. Unfortunately the cost of using ACNTs as adsorbent is expensive limits its commercial utilization on the dot.

All the materials from the supportive studies that have been shown, most of the materials are quite easily available to obtain, just the matter of cost that remains a major problem for commercialization. Therefore, this study will investigate the potential and capability of suggested materials as adsorbent that are oil palm wastes (oil palm fibre and wastes). The selected materials were chosen due to their availability and the possibility of their effective and economic removal of fluoride from drinking water and wastewaters.

2.8) Oil palm wastes potential

As we know, oil palm has a big contribution on economy of Asian countries especially countries that produce products derived from oil palm basis. Palm oil has emerged as one of the most important oils in the world's oils and the market of fats [Mahlia et al., 2001].

According to the chemical composition of dry fiber and shell, as shown in **Table 2.1**, fiber and shell consist of high carbon. With this information, maybe the capability of these adsorbents in their performance of fluoride removal is quite good. Furthermore, a proximate analysis that have been done before shows the properties of shell and fiber generally consist of high fixed carbon as shown in **Table 2.2** [Husain et al., 2002].

Table 2.1: Chemical composition on dry basis of oil palm fiber and shell

ELEMENT	FIBER (%)	SHELL (%)
Hydrogen	6.0	6.3
Carbon	47.2	52.4
Sulphur	0.3	0.2
Nitrogen	1.4	0.6
Oxygen	36.7	37.3
Ash	8.4	3.2

Table 2.2: Approximate properties of solid oil palm wastes

COMPONENT	FIBER (WT %)	SHELL (WT %)
Fixed Carbon	18.8	20.5
Ash	8.4	3.2

In order to make the adsorbents even more effective, perhaps a little modification, pre - treatment or activation may be needed.

Therefore, oil palm wastes can be a good adsorbent for the process of adsorption, objectively to remove fluoride. Besides, they are also easily available and the adsorption process will be very economical because oil palm fiber, sawdust, ash and shell are considered as low cost materials.

3 - METHODOLOGY

3.1 Materials

3.1.1 Adsorbate

A stock solution of fluoride (F^-) with 100 mg/l concentration was prepared using Sodium fluoride (NaF). For the early experiments, most of the time, 20 mg/l of the solutions were used. In order to get a 20 mg/l solutions, 200 ml of stock solution was diluted to 1000 ml with distilled water.

3.1.2 Adsorbents

From all the adsorbents, only ash was used directly in the experiment, and the rest were treated with sulphuric acid 98%. The fibre was obtained from the Palm Oil Research Institution of Malaysia (PORIM). Adsorbents which have been treated with acid were then dried in the furnace for 150^0C, for 24 hours. After 24 hours, the adsorbents were then been washed many times with distilled water about 2000 ml each time washing, until the adsorbents were looked clean and less turbidity. After that, the clean adsorbents were soaked with 1% Sodium Hydrogen Carbonate for 24 hours. Finally, adsorbents were dried in the oven for another 24 hours in 105^0C. After drying process, the adsorbents were ready to be used. Figure 3.1, 3.2, 3.3 and 3.4 show some of the adsorbents used in the experiment.

Figure 3.1 : Treated shell

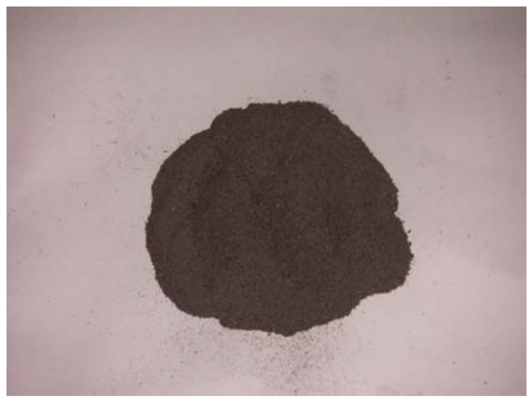

Figure 3.2 : Ash

Figure 3.3 : Treated fibre

Figure 3.4 : Treated sawdust

3.1.3 Equipments/Apparatus

Equipment for weighing is AND – HM 300 was used to measure adsorbents and sodium fluoride. Usually about 500mg of adsorbents were being used at all time.

Figure 3.5 : AND HM-300 weighing instrument

Orbital shaker as shown in Figure 3.6 below was used to shake the samples in the conical flasks. The rpm used for the experiment was 250 rpm.

Figure 3.6 : Orbital shaker

Figure 3.7 shows the pH meter to set pH of the solution and samples before and after shaking.

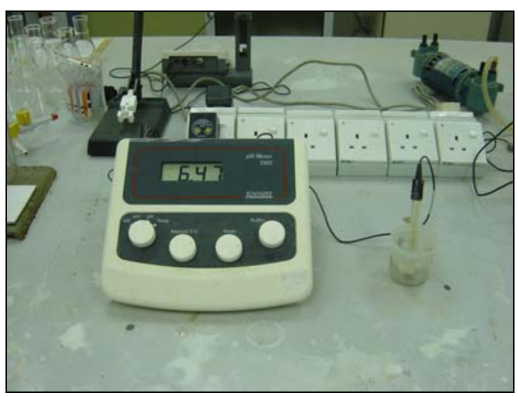

Figure 3.7 : Jenway pH meter 3305

Direct Reading Spectrophotometer (DR 2010) as shown below (Figure 3.8) was used for reading concentration.

Figure 3.8 : DR 2010

3.2 Methods

3.2.1 Adsorbents and Optimum pH Test

a) Twelve conical flasks were filled with 100 ml of fluoride solution. Initial concentration was 20 mg/l.

b) All flasks samples were divided into 3 batches. Batch 1 will be filled with 500 mg of ash. Batch 2 will be filled with 500 mg of fibre and batch 3 will be filled with 500 mg of sawdust.

c) In batch 1, before the adsorbent were filled in, 4 different pH for each one flask and they are pH 1, pH 2, pH3 and pH4 were set. Then, adsorbent were filled into every flask. All samples were then shaken using a mechanical shaker at rpm 250 for 120 minutes.

d) Procedure or steps in c) were applied for batch 2 and batch 3.

e) Each sample was filtered using GF C micro fibre filters.

f) Final fluoride concentrations were measured using DR2010 (Direct Reading Spectrophotometer).

3.2.2 Agitation Time Test

a) Nine conical flasks with 100 ml of fluoride (20 mg/l initial concentration) solution were filled.

b) 500 mg of adsorbent was filled into each flask.

c) All flasks were agitated at 250 rpm using the mechanical shaker.

d) The flasks were taken from the shaker one by one, at 15, 30, 60, 90, 120, 150, 180, 210, and 240 minutes.

e) All samples were filtered using GF C micro fibre filters.

f) Final fluoride concentrations were measured using DR 2010.

3.2.3 Isotherm Equation

a) Nine conical flasks with 100 ml of fluoride (20 mg/l initial concentration) solution were filled.

b) 500 mg of adsorbent was filled into each flask.

c) All flasks were agitated at 250 rpm using the mechanical shaker.

d) The flasks were taken from the shaker one by one, at 15, 30, 60, 90, 120, 150, 180, 210, and 240 minutes.

e) All samples were filtered using GF C micro fibre filters.

f) Final fluoride concentrations were measured using DR 2010.

g) Procedure/steps from a) to f) were repeated but with different initial concentrations which are 40 mg/l, 60 mg/l, 80 mg/l, 100 mg/l, 150 mg/l and 200 mg/l.

4 - RESULTS AND DISCUSSION

4.1) Adsorbent and Optimum pH Test

Three different kind of adsorbents were chosen for the purpose of this experiment and they are ash, treated fibre and treated sawdust. The experiment was a combination of 2 purposes which is to determine the best adsorbent and the optimum pH to remove fluoride. In determining the optimum pH, only 4 different value of pH were chosen. From the previous studies, most of the pH value was used effectively at low pH [Swope and Hess, 1937]. A very good sorption process occurs at pH less than 3. The sorption process is highly pH dependent and is effective at pH values less than 3, and there is a little removal at neutral pH value of 7. Defluoridation by activated alumina was successfully demonstrated (Boruff, 1934., Fink and Lindsay, 1936., Swope and Hess, 1937) and fluoride removal capacity increases directly with fluoride concentration and inversely with pH of the water (Savinelli and Black, 1958). In this project, the experiment was carried out for 2 hours; all samples were shaking at 250 rpm and initial concentration approximately 20 mg/l. From **Table 4.1.(a), Table 4.1.(b) and Table 4.1(c)** it can be observed that ash resulted in the highest (73%) fluoride removal at pH 2.. Thus ash was chosen as the adsorbent in fluoride removal.

Table 4.1.(a): Fluoride adsorption by ash

Adsorbent	Ash			
pH	1	2	3	4
Initial F- Conc. (mg/l)	19	19.4	19.6	19.2
F- Conc. After Test (mg/l)	8.8	5.2	8.2	9.8
% Removal	**54**	**73**	**58**	**49**

Table 4.1.(b): Fluoride adsorption by fiber

Adsorbent	Fiber			
pH	1	2	3	4
Initial F- Conc. (mg/l)	19	19.4	19.6	19.2
F- Conc. After Test (mg/l)	8	8.4	11.6	8.8
% Removal	**58**	**57**	**41**	**54**

Table 4.1.(c): Fluoride adsorption by sawdust

Adsorbent	Sawdust			
pH	1	2	3	4
Initial F- Conc. (mg/l)	19	19.4	19.6	19.2
F- Conc. After Test (mg/l)	10.6	6	10.4	9.4
% Removal	**44.2**	**69**	**47**	**51**