Removal of Fluoride from Drinking Water Using Egg Shells

BY

I NYOMAN PRASETYA PERMANA

13506

A project dissertation submitted to the
Chemical Engineering Program
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

May 2013

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr Lemma Dendena Tufa)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(I Nyoman Prasetya Permana, ID: 13506)

ABSTRACT

Fluoride is one of the ions that naturally occurring and often found in ground or river water both in high and low concentration where its origin might come naturally or anthropogenic. Fluoride in concentration above 1.5 ppm is having a bad side effect to human health since it causes fluorosis that increases the hardness of bones and teeth while reducing their elasticity, thus making the bones brittle.

Removal of fluoride or defluridation is often required in order to reduce the concentration of fluoride in drinking water below its safe level before being consumed. There are many techniques that can be used in order to reduce the concentration of fluoride in water such as adsorption, reverse osmosis, precipitation, and electrodialysis. Adsorption is one of the defluoridation methods that offer low cost and acceptable efficiency without removing other important ions from the water. However its cost and efficiency is highly dependent on its type of adsorbent.

Egg shells, a cheap waste product from food industry, are the chosen adsorbent in this study, where it potential of being an adsorbent of fluoride is being tested by varying the pH and the adsorbent amount. From the study, it is seen that the optimum pH of the adsorption lies at pH around pH5 with highest efficiency of 0.1334942 $mg_{fluoride}/g_{egg\ shell}$. Its capability of regeneration is also being tested and NaOH proven to be the effective reagents for its regeneration process. A further study is suggested on looking at the effect of time od the adsorption amount and also further study regarding which is more feasible between regenerating the used eggshell or replace it with a new one.

ACKNOWLEDGEMENT

I would like to express my utmost gratitude to my very kind and supporting supervisor, Dr Lemma Dendena Tufa for his permission to work on this project and for his assistance throughout the project period. I am thankful to the colleagues and lecturers from chemical engineering department for their support and feed-backs during the progress of this work. In addition to that, I would also like to thank the technicians in chemical engineering department for their help in performing the experiments needed for this study. Last but not least, I would like to thank my family for their continuous support and encouragement in my studies and this project especially.

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CHAPTER 1

PROJECT BACKGROUND

1.1 Background Study

Fluoride is an anion which is the reduced form of fluorine where it acts as an ion or when in is bonded to another element. Like other halides, it is a monovalent ion with -1 charge. Compounds that consist of fluoride usually having distinct properties when compared to other halides compound. Inorganic compound containing fluorine are often called as fluorides. Solutions of inorganic fluoride in water usually contain F^- and HF^{-2}. Only few of the inorganic fluorides are soluble in water without undergoing significant hydrolysis. Because of its smaller radius/charge ratio, fluorides are more strongly solvated thus it reactivity differs from chloride and other halides. When relatively unsolated, fluoride is a very strong base. The presence of fluoride and its compounds can be detected by spectroscopy.

Fluoride is usually found naturally in water and foods, however it exist in low concentration. Average concentration of fluoride in seawater is 1.3 ppm, 0.01-0.3 ppm for fresh water supplies, 1.2-1.5 ppm for ocean (WHO,2004). However some of the fresh water contains a dangerous level of fluoride and defluoridation must be performed in order to remove the excess fluoride from this kind of source.

Fluoride has a good effect on human body at low concentration in drinking water since it promotes calcification and was able to protect tooth from decaying. This beneficial concentration of fluoride in drinking water range from 0.4 ppm to 1.0 ppm (Fawell et. Al, 2006). However if the concentration of fluoride in drinking water is too high, above 1.5 ppm which is stated by World Health Organization (WHO,1996), people who drank the water will be exposed to health problem named fluorosis. Fluorosis is divided into dental fluorosis and skeletal fluorosis. Dental fluorosis is a developmental disturbance of the teeth's enamel caused by overexposure of fluoride. Dental fluorosis happened when the hydroxyapatites, general composition of teeth, in the teeth are replaced by fluorapatites. This causes some white spots on the teeth, in milder case, or a rough brown marking on the teeth in some severe case. The most concern regarding dental fluorosis comes on aesthetic parts in permanent dentition (Yeung,2008).

A more threatening effect of overexposure of fluoride can be seen in the form of skeletal fluorosis which in its advanced cases causes damage and pain to bones and joints. The bones are hardened and become less elastic due to high concentration of fluoride thus resulting in higher frequency of fractures in the bone. On the joints, fluoride promotes the calcification on the joints. Fluorosis also causes thickening of bone structure and accumulation of bone tissue which contributes to impaired joint mobility. On the other hand, high concentration fluorides also affect the thyroid gland which causes hyperparathyroidism where an uncontrolled secretion of parathyroid hormones occurs. These hormones regulate the concentration of calcium in the body thus an increase of these hormones in the body demands an increase in calcium concentration in the body. If the intake calcium is less than the demand caused by this increase in amount of the parathyroid hormones, calcium are started to be taken from the bones thus causes flexibility of the bones reduces. This, combined with the original effect of skeletal fluorosis makes the bones more brittle than it should causing it to easily fractures (Whittford, 1994).

Causes of high fluoride concentration on water are both caused by natural occurrence and industrial activities. Waste water producers such as aluminum, steel, glass, toothpaste, and pesticides industries are often contains fluoride which are able to enter water bodies. While naturally this happened due to the coming of fluoride from some rocks and mineral that contains fluoride and passed by water (WHO,1996). Due to both of this occurrence that increases fluoride level in water, UNICEF stated that there are at least 25 countries which are affected by fluorosis across the globe. Countries that are affected by fluorosis mostly come from Asia, northern Africa, and eastern Africa. Apart from this region there are also some countries that are affected including Mexico, Argentina, Australia and New Zealand. The Figure 1-1 below, which is taken from UNICEF website, clearly shows the countries affected with endemic level of fluorosis (UNICEF).

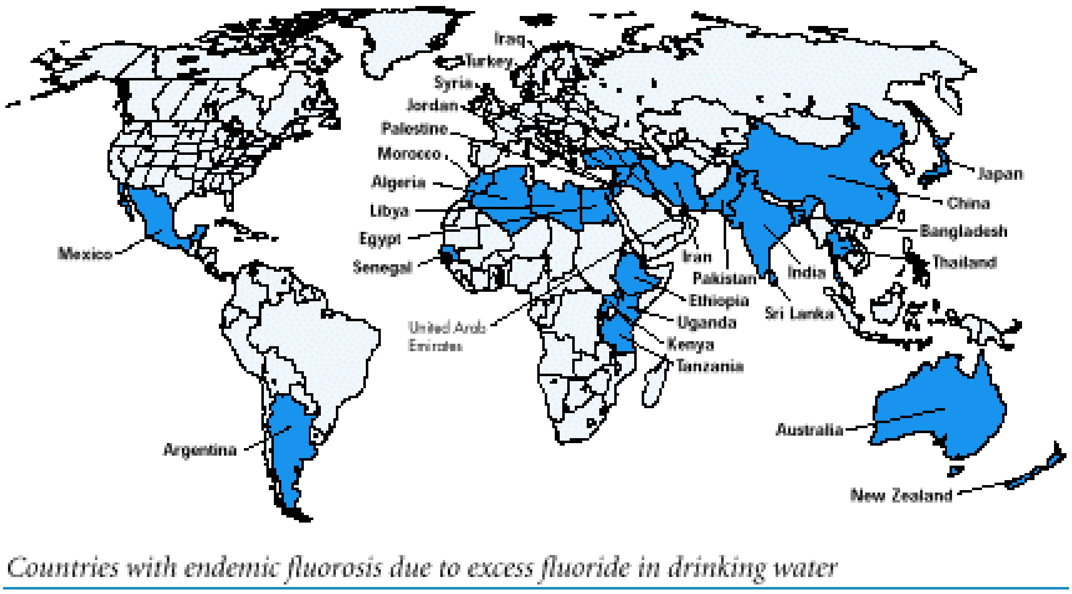

Figure 1-1 Countries with endemic fluorosis

This information above proves that the need of reducing fluoride from water, especially drinking water is becoming more important today.

1.2 Problem Statement

Due to the nature of some water bodies with high fluoride content whether it is because of industrial effect or natural occurrence and the effect fluoride have on human body, it is becoming important to remove this constituent of water to safe level before consumed by people. Removal techniques are being employed in order to reduce the concentration of fluoride. However some of the defluoridation method are expensive are not readily available while giving some setbacks as well as advantage on its own. Egg shells are some example of materials that can remove fluoride from water effectively. Putting it aside, these materials are easily found and needs simple processing before being able to be used for deluoridation process. However, more investigation regarding the capabilities of this material is still need to be done.

1.3 Objective

The objective of the study is as follow:

- To investigate the effectiveness of eggshell as fluoride adsorbent, considering the effect of adsorbent amount and pH.

- Investigate the regeneration capability of eggshell

The study above is done in order to see the feasibility of eggshells as a low cost alternative for defluoridation of drinking water as well as to investigate the regeneration capabilities of eggshell.

1.4 Scope of Study

The basic of the study is about how effective an alternative low cost adsorbent such as eggshells able to remove fluoride from water. First of all the capability of eggshells to remove fluoride from drinking water is being studied by investigating the amount of fluoride it can remove within certain amount of eggshell that is being used. Furthermore, the effect of pH and eggshell amount regarding the capability of the adsorbents and its regeneration capabilities will be investigated to see feasibility of the eggshell to be used on a larger scale.

CHAPTER 2

LITERATURE REVIEW

2.1 Defluoridation Technique

One of the easiest methods in order to reduce concentration of fluoride in drinking water is to add fresh water with lower concentration of fluoride with water with high concentration in order to dilute the fluoride concentration. However, such source of water with low fluoride content might not readily available in some places. Therefore defluoridation is the only alternative left in order to reduce the concentration of fluoride in water. There are five methods that are commonly used to perform defluoridation which are adsorption or ion exchange, electrodialysis, reverse osmosis, and precipitation/coagulation. The advantage and disadvantage of each method are listed on the table below (Logathanan et. al, 2012).

Table 2-1 Comparison of Defluoridation Methods

Method	Advantage	Disadvantage
Adsorption / Ion Exchange	• Most widely used • Cost can be suppressed when using low cost absorbent • Retains effectiveness on low fluoride concentration • Designs are simple and flexible	• Might be costly if high cost absorbent are used, especially ion-exchange resin • Low selectivity against some or all anions. Where anions could be competing with

	• Ease of operation • Minimum to no waste production	fluoride ion • Frequent regeneration or replacement of adsorbent needed • Effective at pH < 7 • Granular adsorbent needed for good hydraulic flow
Precipitation / coagulation	• Medium cost • Precise control of chemicals addition • Widely used	• Low effectiveness, cannot remove below 5mg/L of fluoride due to the high solubility of the product CaF_2 and secondary treatment needed • Requires large amount of chemicals • Frequent testing of feed and treated water needed • Additional cost might come from the chemical, its storage and feeding system • Large volume of sludge waste • Acid neutralization needed

		• Toxic chemicals such as AlF complexes and SO_4 often left in the treated water
Reverse Osmosis	• Excellent removal • No chemicals required • No waste production	• Very high capital and operational cost • Both beneficial nutrients and fluoride are removed • PH dependent • Disposal problem for the residue of concentrated fluoride • Water wasted • Clogging, scaling and fouling problem
Electrodialysis	• Excellent removal • No chemicals required • No waste production	• High capital and operational cost • Both beneficial nutrients and fluoride are removed • Polarization • Need skilled labour

2.2 Principal of Adsorption

Adsorption is the adhesion of atoms, molecules or ions into a surface. These atoms create a film of adsorbate to the surface of the adsorbent (Logathanan et. al, 2012). Mainly there are five mechanism in which adsorption occurs which are van der Waals force, ion exchange, hydrogen bonding, ligand exchange, and chemical modification on the surface of adsorbent. In the case of adsorption of fluoride, van der Waals and ion exchange mechanism both uses weak physical adsorption an not specific to fluoride. However hydrogen bonding and ligand exchange could give a more specific adsorption of fluoride since it is governed by chemical adsorption. Modification on the surface of adsorbent gives both chemical and physical adsorption thus giving both specific and non-specific adsorption.

If other anions existed in the water, both van der Waals and ion exchange cannot remove fluoride easily. Fluoride adsorption however, will be achieved by hydrogen bonding and ligand exchange in the presence of most types of anions in the water. Only some anions that specifically on the adsorbent will compete with fluoride on the adsorption sites (Logathanan et. al, 2012).

Van der Waals force is weak and only applies on short range. This force is proportionally increasing with the size of the molecules involved. Therefore adsorbates with high molecular weight will be more likely to stick on the surface of an adsorbent. Therefore this causes fluoride will be hard to be removed from solution which contains another adsorbate that have higher molecular weight, for example organic matters (Gupta et al, 2006). Only manganese oxide-coated alumina at high pH is able to adsorb fluoride via van der Waals force (Teng et all, 2006).

In ion exchange, occurs a stoichiometric process where ions leaving ion exchanger surface is replaced by equivalent number of moles of ions in order to maintain the neutrality of the exchanger where this process is rapid and reversible. Ion exchange selectivity depends on the valency, concentration and size of the ions that is involved in the exchange. Higher valency, higher concentration and smaller hydrated equivalent volume are favored. Fluoride removal is hard to achieve via this mechanism due to the fact that there are many other anions which are having better selectivity compared to fluoride. This selectivity order can be simplified as the following: citrate > SO42- > I- > NO3- > CrO42-> Br- > SCN- > Cl- > acetate > F-. Thus if these anions exist in the solution, it will be very hard to selectively adsorb fluoride (Weinerl, 2012).

Hydrogen bonding gave a strong dipole-dipole attraction between the strong electropositive H atom in a molecule of an adsorbent and a strong electronegative atom in another molecule (Weinerl, 2012). This type of bond gives a strong force compared to van der Waals and ion exchange but weaker than ligand exchange. Due to its high charge/atomic radius value, fluorine is one of the most electronegative atom thus is having high selectivity on adsorption. Coal based adsorbent and ion exchange resins are examples of adsorbent which create hydrogen bond with fluoride (Sivasamy, 2011).

Taking a look on ligand exchange mechanism, metallic cation at the surface of an adsorbent creates a strong covalent metallic bond with fluoride in solution. This releases other potential determining ions that were bound to the metallic cation before such as OH-. Therefore F is specifically adsorbed on the adsorbent surface or sometimes called as forming inner sphere complex. This ligand exchange mechanism, expecially on metal oxides, often cause an increase in the pH of the solution because of the release of OH- ions from the adsorbent. This kind of adsorbent has an advantage in terms of giving high adsorption capacity as well as high selectivity. Ligand exchange mechanism also enables the adsorbent to remove a large proportion of anions which have higher selectivity but lower concentration in a solution where competing anions with lower selectivity but higher concentration also existed (Tokunaga et al, 1995).

Adsorption capacity of an adsorbent can be improved by performing chemical modification on the surface of the adsorbent. This is useful especially in the case where the adsorbents are having negative surface charge which might repel the negatively charged fluoride. In these kind of adsorbents, positive charged multivalent cations are introduced into the adsorbent in order to attract fluoride ions by columbic force and produce adsorption sites that can interact with the fluoride ions. These cations act similar like a bridge to assist the adsorption.

Therefore it can be concluded that among these methods, the best solutions for adsorption in defluorization of water is by harnessing the ligand exchange and hydrogen bonding mechanism. And further studies have found out that ligand exchange mechanism are dominant when inorganic adsorbent were used, where hydrogen bonding were dominant when organic adsorbent were used (Logathanan et. al, 2012)

Adsorption rate and capacity are affected by several factors including pH, temperature, adsorption kinetics, and co-existing anions. Among these factors, pH is considered as the factor that has greatest effect to adsorption. Adsorption reaches its lowest value on both very low and very high pH. Despite that each type of adsorbent has their own optimum pH, but they can be generalized as having good performance at the pH ranging from 4 to 8. This occurs due to the concentration of positive when pH is low and negative ions when pH is high. The reduction of adsorption below pH 4 occurs because fluoride started to react with hydrogen to form weakly ionized HF. At pH higher than 8, the surface of the adsorbent started to become negatively charged, thus hindering attraction of fluoride. Furthermore high pH condition causes other competing cations increases in number which further lessen the adsoption capability (Logathanan et. al, 2012).

Some anions like phosphate, chloride, sulphate, bromide and nitrate presents in natural water and having potential of competing with fluoride for removal by adsorbents. However this competition only depends on the relative concentration of these ions and their affinity for the adsorbent (Meenakshi & Viswanathan, 2007). Mostly they will affect the adsorption when ion exchange resins are used as an adsorbent. Past studies shows that nonspecifically adsorbing ion, such as nitrate and chloride, doesn't have effect on fluoride adsorption that is using adsorbent that specifically adsorb fluoride. Only specifically adsorbed anions such as phosphate, arsenate and selenate can compete with fluoride in this kind of adsorbent. However, if a non-specific adsorbent is being used, both nonspecifically and specifically adsorbed anions can compete with fluoride (Logathanan et. al, 2012).

Different with earlier factors, temperature shows now consistency in terms of its effect on adsorption. Adsorption with endothermic nature increases as temperature increases, however it decreases as temperature increase if an exothermic natured adsorption occurs (Logathanan et. al, 2012). Some adsorbents, like trivalent cations/zeolite, show no significant effect on adsorption when temperature is changed (Onyago et all, 2004). The reason of this inconsistencies are not well investigated and stated in previous studies since it may depends on temperature range studies, the nature of the adsorbent, and the conditions used in the studies (Logathanan et. al, 2012).

Finally adsorption kinetics also has its own effect on adsorption. Studies have shown that 90% of fluoride was removed in the first 5-120 minute where the rate of removal was very high at this range and thereafter falls off significantly and finally approaches zero as the sign of equilibrium. This occurs because at the early minutes, there are many vacant sites on the adsorbent thus encourage high rate of removal. This fast rate enables the adsorbent to treat large quantity of water (Lv et. al, 2006) where slow rate would be a problem in the adsorption process of the filter bed (Ruixia, Jinlong & Honxiao, 2002). Rate of fluoride adsorption increases as the initial concentration of adsorbent increases (Lv et. al, 2006) and as the initial concentration of fluoride decreases. Properties of the structure of the adsorbent and the interaction of fluoride with these sites also determine the rate of reaction (Logathanan et. al, 2012).

Suitable adsorbent for fluoride doesn't just have a good capability in adsorbing fluoride. It also need good cost effectiveness as well as good desorption capabilities, where the latter could lead into efficient regeneration for multiple times. A good reagent for desorption or regeneration process doesn't damage the adsorbent. Desorption occurs by leaching the fluoride ion from the adsorbent by the action of salts, acid or bases. Desorbing agents can be chosen based on the activity of the adsorption at certain pH. Low adsorption on low pH proposes acid as the desorbent and low adsorption at high pH proposes bases as the desorbent. Therefore the optimum desorption condition is basically on the lowest condition for adsorption. (Logathanan et. al, 2012).

2.3 Egg Shell

The outer coatings of hard-shelled eggs are often called as egg shell. Avian egg shells existed in order to protect the egg against damage and contamination. It also provides calcium for embryogenesis. According to the data from US food industry, more than 150000 tons of egg shell waste was produced in a year. Where mostly used as fertilizer, animal feed ingredients or discarded (Nakano, Ikawa & Ozimek, 2003). Egg shells, especially bird ones, contains calcium carbonate inside it. Chicken eggshells are made of 94% calcium carbonate crystals where it is stabilized by a protein matrix. The remaining constituents are made of magnesium carbonate by 1%, calcium phosphate for 1% and organic matter, which includes the protein matrix, by 4%. The egg shells waste from food processing and manufacturing usually composed of the calcium carbonate and the eggshell membrane or called as

ESM. The ESM resides between the egg white and the inner surface of the eggshell (Parsons, 1982; Nakano, Ikawa & Ozimek, 2003).

Egg shell powder also start being used as a fluoride adsorbent from ground water due to its high calcium content that can attract the negative fluoride ions. Experimental data indicated monolayer sorption of homogeneus surface. And according to Dubinin-Radishkevic isotherm model, the adsorption mechanism of eggshell powder was chemisorption. This was implied by the kinetics of the adsorption by eggshell which follows a pseudo-second-order kinetic model. Thermodynamic model also implies that adsorption of fluoride by egg shells are exothermic and spontaneous process. Eggshell powder also found to have a good result when tested to defluoride ground water sample collected from Nasipur and Nowapara Village in India (Bhaumik et. al, 2012).

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

3.1.1 Chemical and Materials Needed

Some chemicals and materials needed for the study are:

- Eggshells

Eggshells will be the main material to be studied. The material however will be treated 1st before being used to conduct experiment.

- Sodium Fluoride

Sodium fluoride will be the basis for the fluoride solution. The initial solution concentration will be based on 5mg/L and 10mg/L with the amount of 200mL.

- Phosporic Acid

Phosporic Acid will be the main acid used to backwash the eggshell powder to investigate its regeneration capabilities

- HCL

Hydrochloric acid will be used to conduct experiment regarding the effect pH on the adsorption. It will be prepared to alter and prepare the pH of the solution.

- NaOH

Hydrochloric acid will be used to conduct experiment regarding the effect pH on the adsorption. It will be prepared to alter and prepare the pH of the solution. A solution of 0.01 Mol NaOH will be prepared to regenerate the eggshell as well.

3.1.2 Experimental Procedures / Approach

The figure 3-1 below will show the experimental procedure that will be implemented in this study

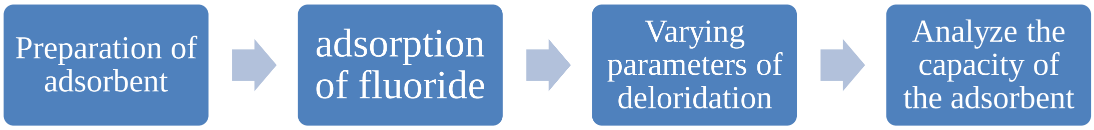

Figure 3-1 Experimental Approach

Furthermore, to investigate the regeneration capability of eggshell, the remaining eggshell after the it is saturated with fluoride will be backwashed with mild acid such as phosphoric acid and will be tested again with similar approach with the above figure.

3.2 Preparation of Adsorbent

The preparation of the eggshell powder will be done based on the following procedure:

- The eggshells will be washed will distilled water
- The eggshells will be put into oven at 100 C and left overnight (12hours)
- The eggshells then will be ground using mortar and pestle

3.3 Preliminary Experiment

The procedure for testing the effect of the amount of adsorbent used will be done based on the following procedure:

- 200 mL of 2.15 mg/L of fluoride solution will be put into 4 1L beakers. Their pH are being controlled using HCl and were put into pH of 3.
- 1.4, 2.8, 4.2 and 5.6 grams of adsorbent were put into the beakers respectively. Using jar test equipment, the solution is stirred for 2 hours under 120 rpm.
- After 2 hours, 10ml of solutions from each beaker are extracted and put into different test tubes. Ion chromatography was used to determine the final value of the fluoride concentration.
- The experiment was then repeated using absorbent values of 0.28, 0.56, 0.84 and 1.12 g .

3.4 Testing the Effect of pH and Amount of Adsorbent at 5mg/L solution

The procedure for testing the effect of pH will be done based on the following procedure:

- 200 mL of 5mg/L of fluoride solution will be put into beakers, the pH and amount of the adsorbent will put accordingly as described in table 3-2 below.
- Beakers will be put into jar test equipment to induce stirring.
- The experiment is done when t=120 minutes. A sample from the end solution will be taken to be measured of its fluoride content

Table 3-1 Taguchi L'16 Array

Experiment	Amount of eggshell	pH	Result (q_e)
1	1.5	3	
2	2.4	3	
3	3.3	3	
4	4.2	3	
5	1.5	5	
6	2.4	5	
7	3.3	5	
8	4.2	5	
9	1.5	7	
10	2.4	7	
11	3.3	7	
12	4.2	7	
13	1.5	9	
14	2.4	9	
15	3.3	9	
16	4.2	9	

3.5 Testing Effectiveness at Higher Concentration of Fluoride

The procedure for testing the effect of the amount of adsorbent used will be done based on the following procedure:

- 200 mL of 10 mg/L of fluoride solution will be put into 4 1L beakers. Their pH are being controlled using HCl and were put into pH of 5.
- 1.5, 2.4, 3.3 and 4.2 grams of adsorbent were put into the beakers respectively. Using jar test equipment, the solution is stirred for 2 hours under 120 rpm.

- After 2 hours, 10ml of solutions from each beaker are extracted and put into different test tubes. Ion chromatography was used to determine the final value of the fluoride concentration.

The experiment was then repeated using absorbent values of 0.28, 0.56, 0.84 and 1.12 g .

3.6 Testing the Regeneration Capability

The procedure for testing the regeneration capabilities will be done based on the following procedure:

- 1.5 g of dried and used adsorbent will be prepared.
- The adsorbent will be left overnight on oven at 110 C
- 200 mL of 5mg/L of 0.01MOL phosphoric acid is prepared as well as 0.01MOL of acetic acid and 0.01MOL of NaOH. A 200mL of distillled water is prepared as well.
- The used adsorbent will be added to the solution. The beaker then put into jar test equipment the timer then started.
- The experiment is done when t=120 minutes.

3.7 Variation of Parameter

The effects of the parameters that will be investigated includes the effects of pH and amount of the adsorbent. Other parameters will be kept constant when one of the parameters is being tested. A further look on the effect of time and adsorption rate is proposed to be investigated as well.

3.8 Key Milestones

Table 3-2 Key Milestones

No	Milestone	Date 2013
1	Completion of Extended Proposal	25th February
2	Completion of Proposal Defense	14th March
3	Submission of Interin Report	22nd April
4	Completion of testing effect of preliminary experiment	5th July
5	Completion of determining the effectiveness of Eggshell	25th July
6	Completion of the regeneration capabilities	1st August
7	FYP Final Report 1st Draft	15th August
8	Completion of Final Presentation	26th August
9	Completion of dissertation	13 September

3.9 Gantt Chart

Table 3-3 Gantt chart

NO	DETAIL	Week																											
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	Selection of Project Title	■	■	■																									
2	Preliminary Research Work and Literature Review			■	■	■	■																						
3	Submission of Extended Proposal							■																					
4	Preparation for Oral Proposal Defence								■	■																			
5	Oral Proposal Defence Presentation									■																			
6	Detailed Literature Review									■	■	■	■																
7	Preparation of Interim Report									■	■	■	■																
8	Submission of Interim Draft Report														•														
9	Submission of Interim Final Report														•														
10	Detailed Methodology									■	■	■	■	■	■														
11	Experiment															■	■	■	■	■	■								
12	Results analysis and Discussion																		■	■	■	■	■	■					
13	Conclusion and Compiling																					■	■	■	■	■	■		
14	Preparation for final presentation																							■	■	■	■		

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary Experiment

Due to the impurity of the sodium fluoride, the solution used for preliminary experiment was supposed to be 5mg/L of fluoride. However impurity of the solid NaF caused the resulting solution made after dilution was 2.14 mg/L. the result of the experiment are shown on the table 4-1 below

Table 4-1 Result of Preliminary Experiment

Amount of adsorbent	Starting Fluoride concentration (mg/L)	Final Fluoride concentration (mg/L)	Fluoride Removed (mg)	Fluoride Removed/ adsorbent used q_e (mg/g)	Concentration Change/ adsorbent used Q_e (mg/g)
0.28	2.5	2.095	0.055	0.19642	1.44642
0.56	2.5	2.058	0.092	0.16428	0.78928
0.84	2.5	2.037	0.113	0.13452	0.55119
1.12	2.5	2.012	0.138	0.12321	0.43571
1.4	2.5	1.986	0.164	0.11714	0.36714
2.8	2.5	1.936	0.214	0.07642	0.20142
4.2	2.5	1.986	0.164	0.03904	0.12238

5.6	2.5	1.924	0.226	0.04035	0.10285

Some graph (Figure 4-1,4-2,4-3,4-4) can be plotted from this results, which are the amount of adsorbent vs final fluoride concentration, fluoride removed, amount of adsorbent vs % removal, amount of adsorbent vs mg fluoride removed/g eggshell used like shown below.

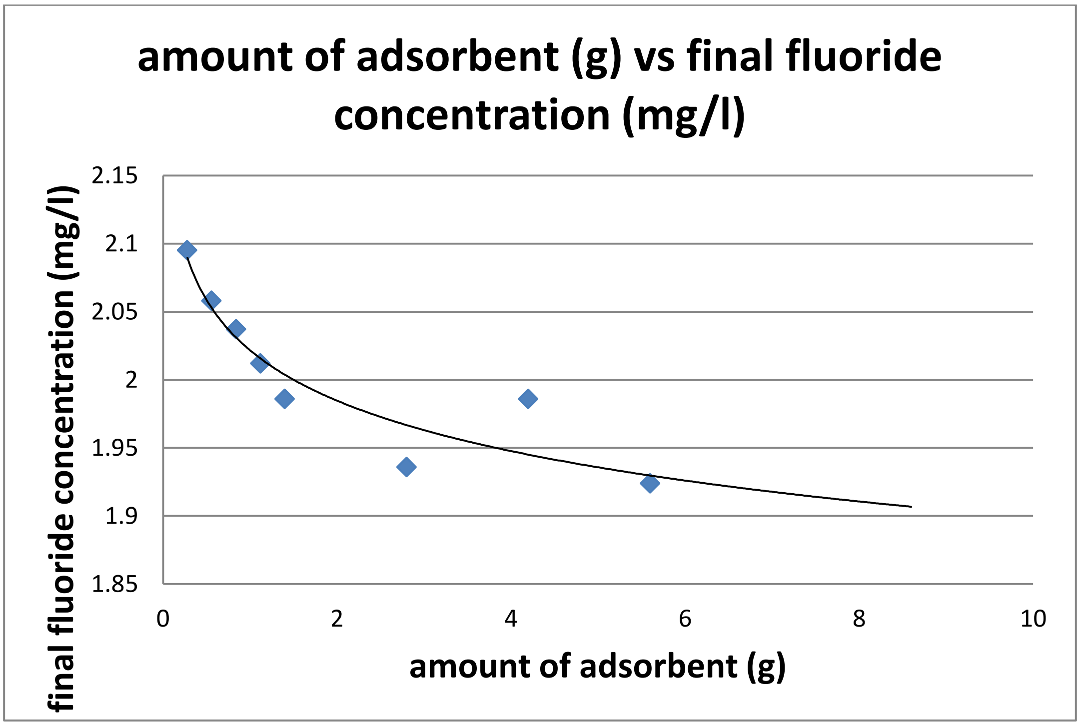

Figure 4-1 Amount of eggshell vs final fluoride concentration

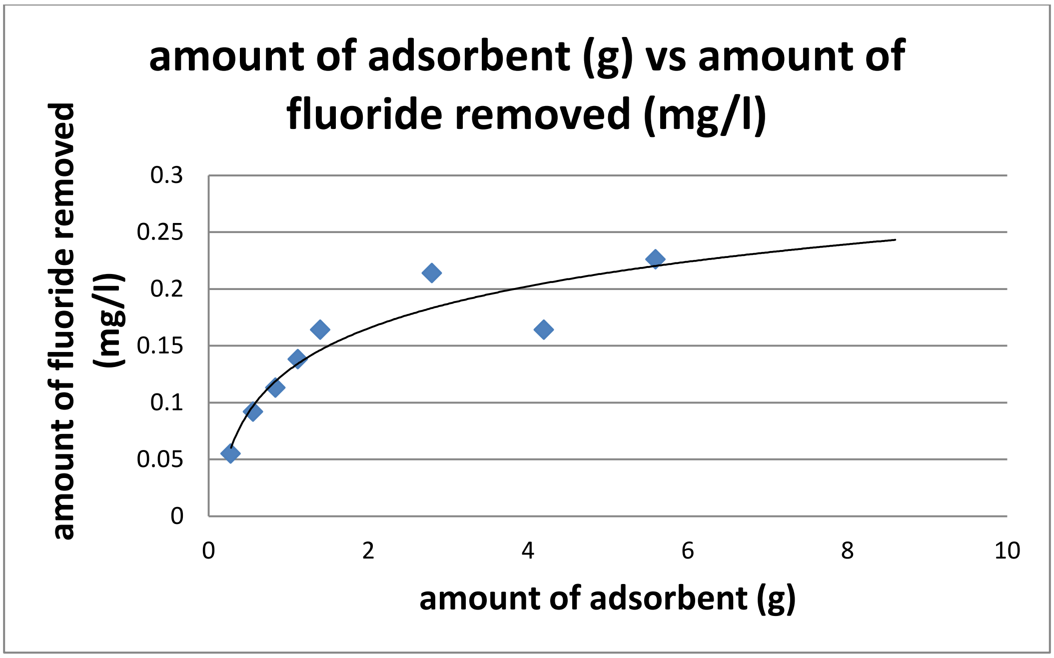

Figure 4-2 Amount of eggshell vs amount of fluoride removed

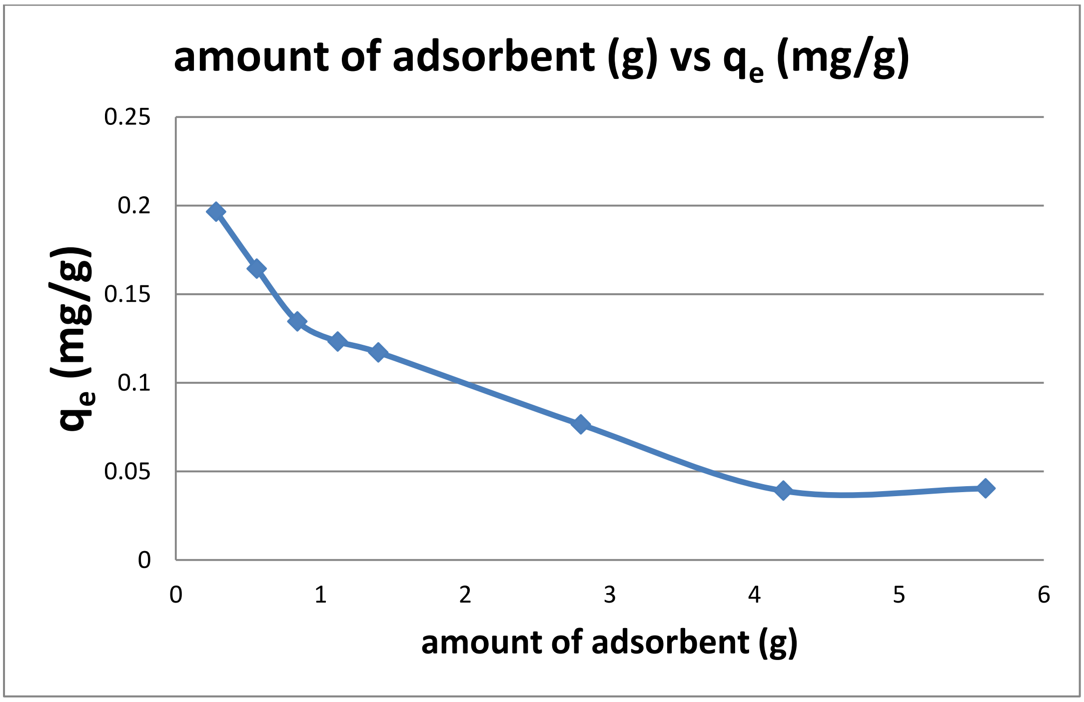

Figure 4-3 Amount of adsorbent vs q_e

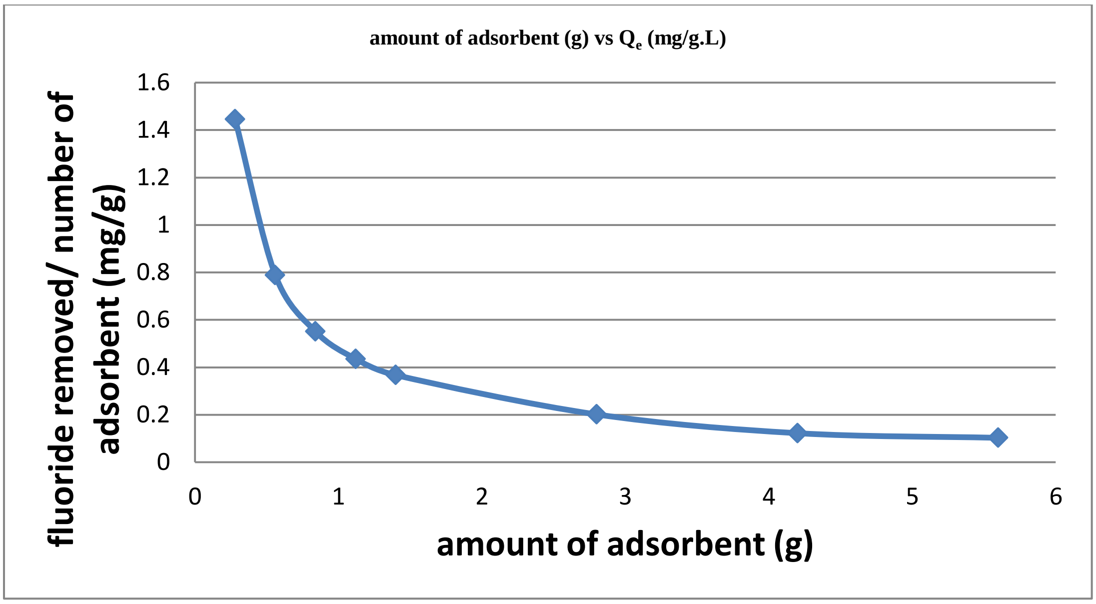

Figure 4-4 Amount of adsorbent vs Qe

From the table and result of this preliminary experiment a further information can be deduced. 1st of all, it can be clearly seen that the adsorption of fluoride at pH of 3 proven to have its own equilibrium. From the preliminary experiment it can be seen that the adsorption somehow getting slower when it reaching the concentration of 1.9 mg/L. Therefore it can be determined that the adsorption of fluoride at pH 3 by eggshell have its equilibrium state somewhere at concentration of 1.9mg/L.

Another interesting finding is that the higher value of qe or the amount of fluoride adsorbed/amount of eggshell reaches its highest value around 0.08 mg/g. however its optimum value is yet to be determined due to the accidentally small concentration used in this preliminary experiment. Compared to the findings by Bhaumix et. Al (2012), this value is relatively small. Where in the article it is shown that the qe value could reach up to around 0.19 mg/g for solution of 5mg/l while for solution of 20mg/l it can reaches up to 0.75 mg/g.

The results of the preliminary experiment can be proven useful in order to determine the right dose to be experimented on the main experiment. By using the equilibrium value and the dose extracted from the article by Bhaumik et al (2012) and from the preliminary experiment.

At pH 3, therefore the amount of fluoride that can be absorbed before reaching equilibrium is

5mg/l-1.9mg/l*0.2L= 0.62mg

Thus by applying the dose both from preliminary experiment and Bhaumik et al (2012) the needed amount of adsorbent will be

0.62 mg / 0.04 mg/g = 16 g

0.62 mg/ 0.19 mg/g = 3.3 g

Since the main experiment will follow a taguchi method and will follow the L'16 array, 4 different parameter of the amount of adsorbent will be needed. However, this is only based on pH of 3. Since the experiments done in the reference article of this study (Bhaumix et al, 2012) were mainly done using adsorbent with the amount of 2.4 and since the difference in amount based on the preliminary experiment was too big compared to dose suggested amount, the amount gained from preliminary experiment was neglected. Thus the selected amount of adsorbent to be used on the main experiment will be around 2.4 mg and 3.3 mg with additional two levels are added by subtracting and adding by the same amount of differences therefore the chosen amount were 1.5g, 2.4g, 3.3g, and 4.2 g of eggshells. Therefore this further modifies the taguchi L'16 array into Table 3-1.

4.2 Testing the Effect of pH and Amount of Adsorbent at 5mg/L solution

By using the results gained from the preliminary experiment. A proper taguchi L'16 array was formed in order to test the efficiency of eggshell as a fluoride adsorbent in the effect of changing pH and adsorbent amount. The result of the experiment is shown on the table 4-2 below.

Table 4-2 Effect of pH and Amount of Adsorbent at 5mg/L solution

Experiment	Amount of eggshell (g)	pH	Change in Fluoride Concentration (mg/L)			
			Reading 1	Reading 2	Reading 3	Average
1	1.5	3	0.9425	0.9424	0.9425	0.9425
2	2.4	3	1.3914	1.3913	1.3914	1.3914
3	3.3	3	1.6965	1.6966	1.6966	1.6966
4	4.2	3	1.8680	1.8680	1.8680	1.8680
5	1.5	5	1.1010	1.1010	1.1010	1.1010
6	2.4	5	1.7267	1.7266	1.7266	1.7266
7	3.3	5	2.1331	2.1130	2.1130	2.1130
8	4.2	5	2.5040	2.5040	2.5040	2.5040
9	1.5	7	0.9030	0.9032	0.9032	0.9032
10	2.4	7	1.3552	1.3551	1.3553	1.3552
11	3.3	7	1.5143	1.5145	1.5143	1.5143
12	4.2	7	1.3683	1.3682	1.3683	1.3683
13	1.5	9	0.4617	0.4617	0.4617	0.4617
14	2.4	9	0.8392	0.8392	0.8391	0.8392
15	3.3	9	1.3065	1.3063	1.3064	1.3064
16	4.2	9	1.6823	1.6821	1.6823	1.6823

Based on the data from the table 4-2, table 4-3 is below done in order to draw out the most important factors regarding the efficiency of eggshell. The desired responses are put into terms or fluoride removed/ adsorbent used and change in concentration/amount of adsorbent used. A sample calculation to find the amount of fluoride removed is shown below

$$Fluoride\ removed = concentration\ change\ x\ 0.2\ L =$$
$$= 0.9425\ x\ 0.2 = 0.1185\ \text{mg}$$

By dividing the gained value of concentration change and fluoride removed with adsorbent amount, the effectiveness in terms of concentration change/g of adsorbent used and fluoride removed/g of adsorbent used is gained and shown on table 4-3.

Table 4-3 Effectiveness of Eggshell at 5mg/L

Experiment	Amount of eggshell (g)	pH	Fluoride Removed (mg)	Fluoride Removed/adsorbent used q_e (mg/g)	Concentration Change/ adsorbent used Q_e (mg/g)
1	1.5	3	0.1885	0.1257	0.6283
2	2.4	3	0.2783	0.1159	0.5797
3	3.3	3	0.3393	0.1028	0.5141
4	4.2	3	0.3736	0.0890	0.4448
5	1.5	5	0.2202	0.1468	0.7340
6	2.4	5	0.3453	0.1439	0.7194
7	3.3	5	0.4226	0.1281	0.6403
8	4.2	5	0.5008	0.1192	0.5962
9	1.5	7	0.1806	0.1204	0.6021
10	2.4	7	0.2710	0.1129	0.5647
11	3.3	7	0.3029	0.0918	0.4589
12	4.2	7	0.2737	0.0652	0.3258
13	1.5	9	0.0923	0.0616	0.3078
14	2.4	9	0.1582	0.0659	0.3297
15	3.3	9	0.2613	0.0792	0.3959
16	4.2	9	0.3365	0.0801	0.4006

By using Design Expert, the data gained above was analyzed on the basis of using Q_e as response.

The resulting ANOVA table is shown at Table 4-4 below

Table 4-4 ANOVA Table

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	0.235980362	6	0.03933006	7.947885328	0.0034
pH	0.196800529	3	0.065600176	13.25659498	0.0012
Amount	0.039179832	3	0.013059944	2.63917568	0.1133
Residual	0.044536443	9	0.004948494		
Cor Total	0.280516805	15			

And since the model value of F is 7.95 therefore it is significance and the chance of noise causing this value to be this big is only 0.34%. another significance is showed by the value of “Prob>F” where a value lower than 0.05 indicate the model term is significant. In this case pH and amount of adsorbent are significant model term.

The resulting graph on the effect of pH on the efficiency of eggshell can be seen from the figure 4-5 below. However it is need to be noted that the graph is based on the averaged value which is gained from individual graph of specific adsorbent amount.

From the figure, it can be clearly seen that the optimum pH for the adsorption is at the pH of 5 with averaging value of 0.672471 mg/L.g or 0.1344942 $mg_{fluoride}/g_{egg\ shell}$.

This optimum pH value is only slightly different from the previously gained value by Bhaumik et al (2012) which peaked at the pH of 6.

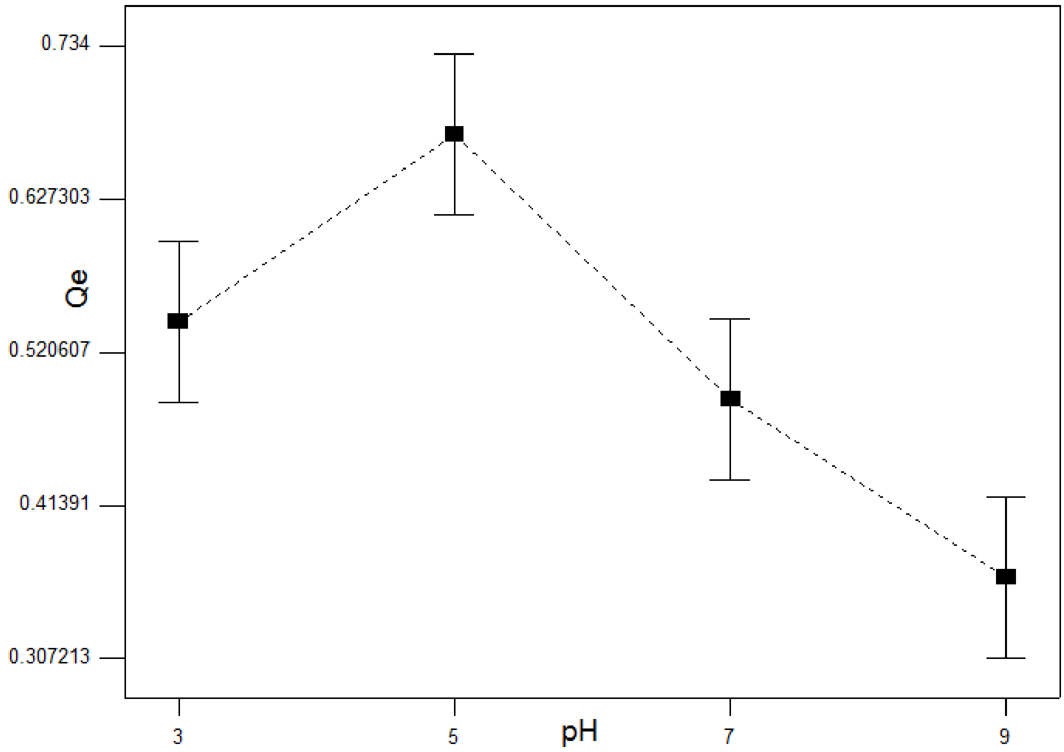

Figure 4-5 Effect of pH on adsorption efficiency (averaged amount of adsorbent)

The effect of the amount of adsorbent used on the efficiency of the eggshell adsorbed is shown on the Figure 4-6 to Figure 4-9 below.

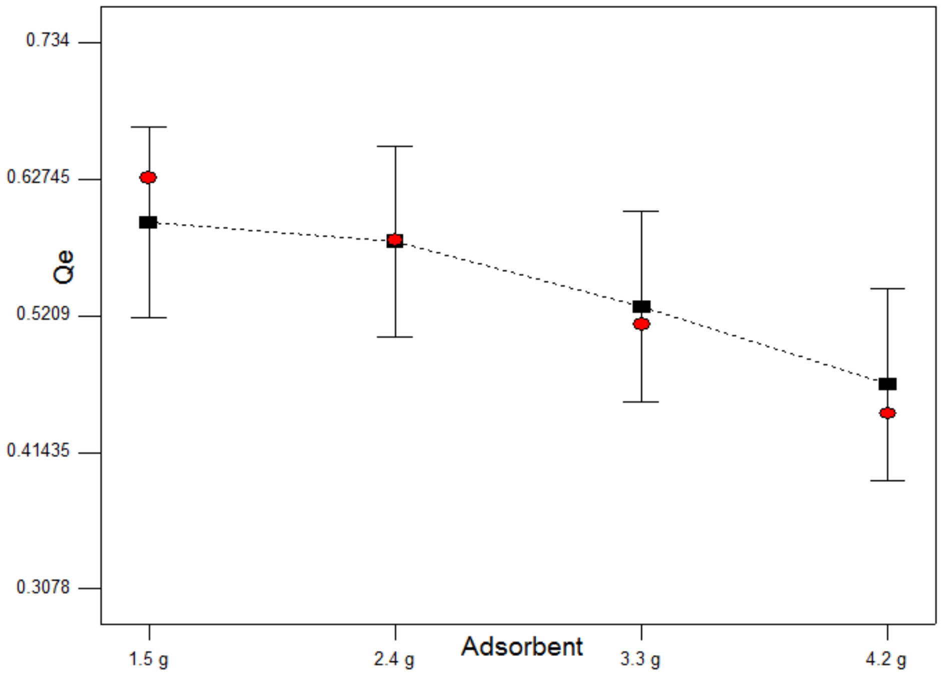

Figure 4-6 Effect of amount of adsorbent on adsorption efficiency at pH 3

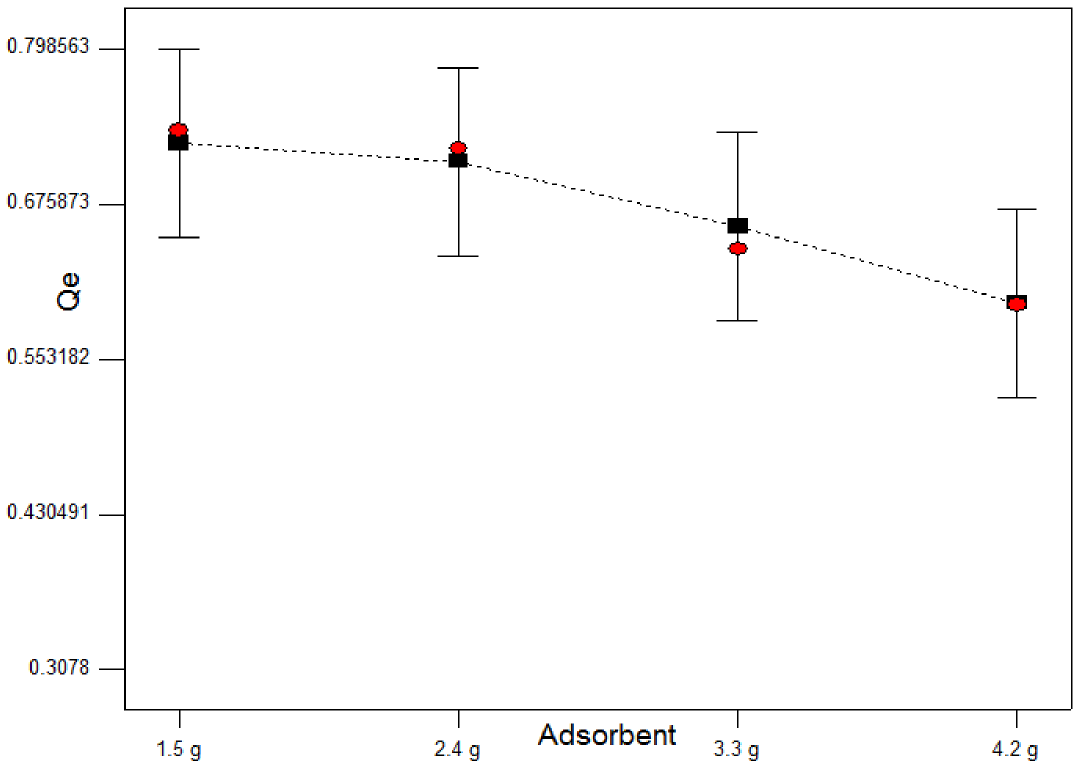

Figure 4-7 Effect of amount of adsorbent on adsorption efficiency at pH 5

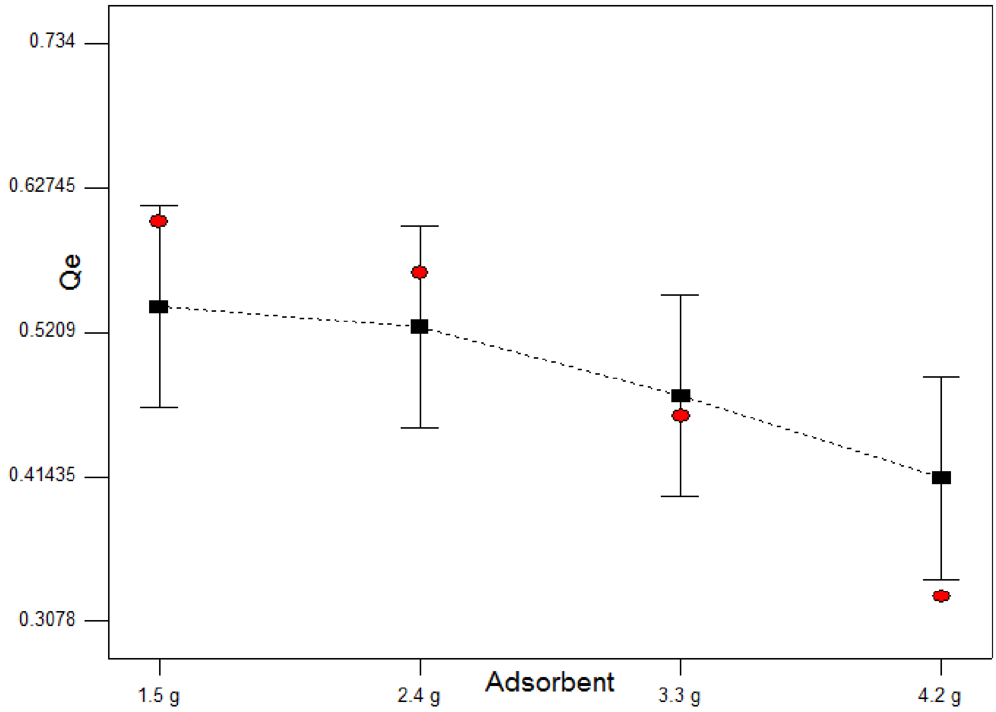

Figure 4-8 Effect of amount of adsorbent on adsorption efficiency at pH 7

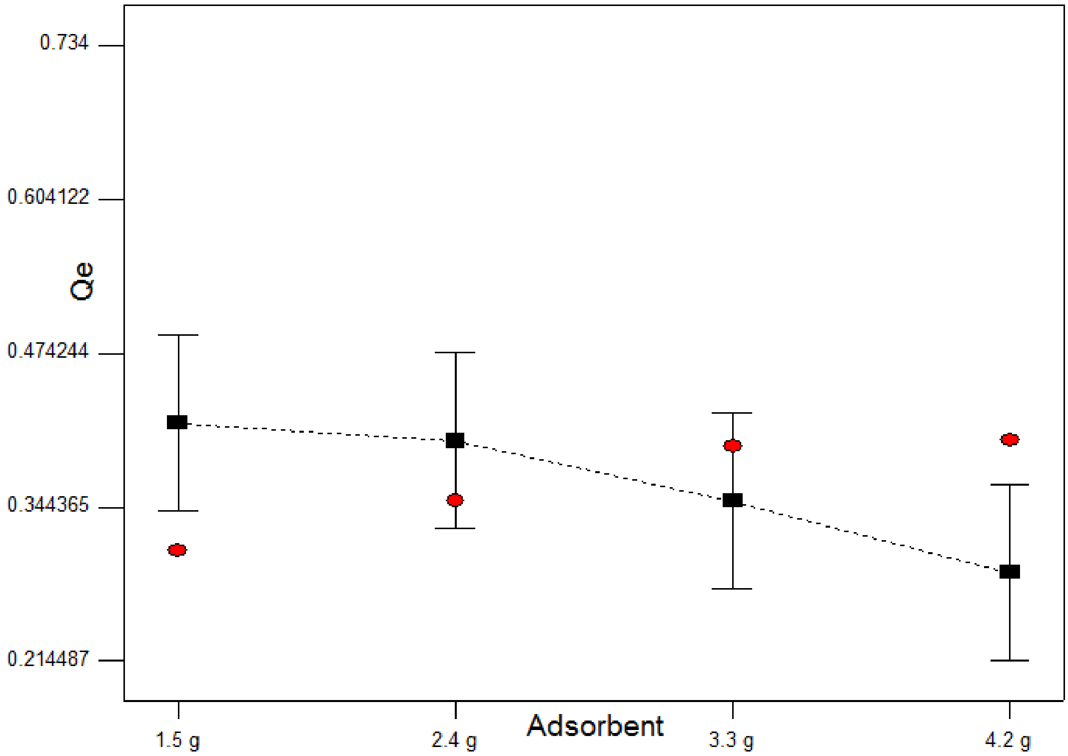

Figure 4-9 Effect of amount of adsorbent on adsorption efficiency at pH 9

The figure was taken from the resulting calculation of the Design Expert software, where the red dots are the input values gained from experiment and the dark lines are the values gained after analyzing by design expert. From the figure it is shown that the efficiency usually peaked at the value of adsorbent around 1.5 grams when applied to 200 ml of 5mg/L solution of fluoride under room temperature and 200 rpm. This value agrees on the past study by Bhaumik et al (2012) which shows that the adsorption value peaked around 1.5 grams where higher amount of the adsorbent showed to have constant value to of efficiency.

The slight difference in the trend could happened because of the hindrance experienced by the greater amount of eggshell due to the lower rpm applied, which was 200 rpm compared to 250 rpm used on the previous study by Bhaumil et al (2012). Another caused might be the type of the mixer used was unable to perform a complete stirring. From the data gained, it is also found that the maximum amount of adsorption efficiency was 0.697242 mg/L.g or 0.1394484 $mg_{fluoride}/g_{egg\ shell}$. The lower rpm, egg shell particle size and the mixer type might also be the source of the slight differences with the past study by Bhaumix et al (2012). The Figure 10 below shows the compiled graph on the effect of amount of adsorbent on different pH level.

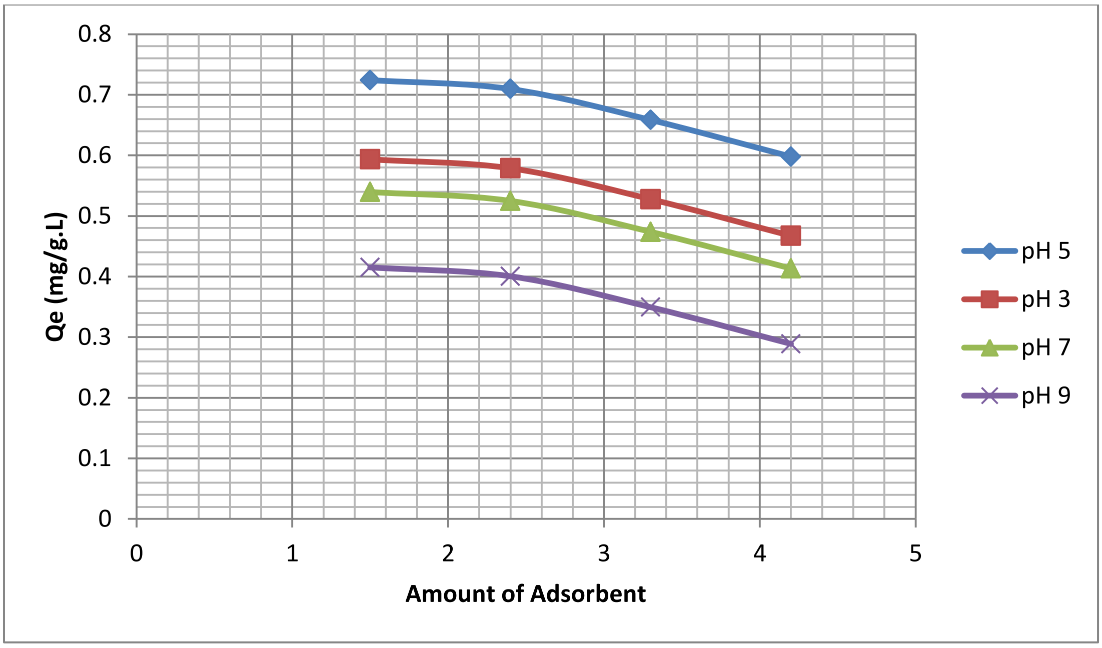

Figure 4-10 Effect of amount of adsorbent on different level of pH

4.3 Testing Effectiveness at Higher Concentration of Fluoride

A similar test was done on a higher level concentration of fluoride in order to see any changes happening in the adsorption trend or values. The pH chosen to be tested was at pH 5 with rpm 200, concentration of fluoride at 10 mg/L with 200 ml solution. The result is shown on the Table 4-5 below and plot on Figure 4-11 below.

Table 4-5 Concentration Change at 10mg/L Fluoride solution

Experiment	Amount of eggshell (g)	pH	Change in Fluoride Concentration (mg/L)			
			Reading1	Reading2	Reading3	Average
1	1.5	3	1.5550	1.5552	1.5554	1.5552
2	2.4	3	2.4274	2.4271	2.4274	2.4274
3	3.3	3	3.2388	3.2385	3.2385	3.2386
4	4.2	3	3.8405	3.8405	3.8404	3.8405

Table 4-6 Effectiveness at 10mg/L fluoride solution

Experiment	Amount of eggshell (g)	pH	Fluoride Removed (mg)	Fluoride Removed/adsorbent used q_e (mg/g)	Concentration Change/ adsorbent used Q_e (mg/g.L)
1	1.5	3	0.3110	0.2074	1.0368
2	2.4	3	0.4855	0.2023	1.0114
3	3.3	3	0.6477	0.1963	0.9814
4	4.2	3	0.7681	0.1829	0.9144

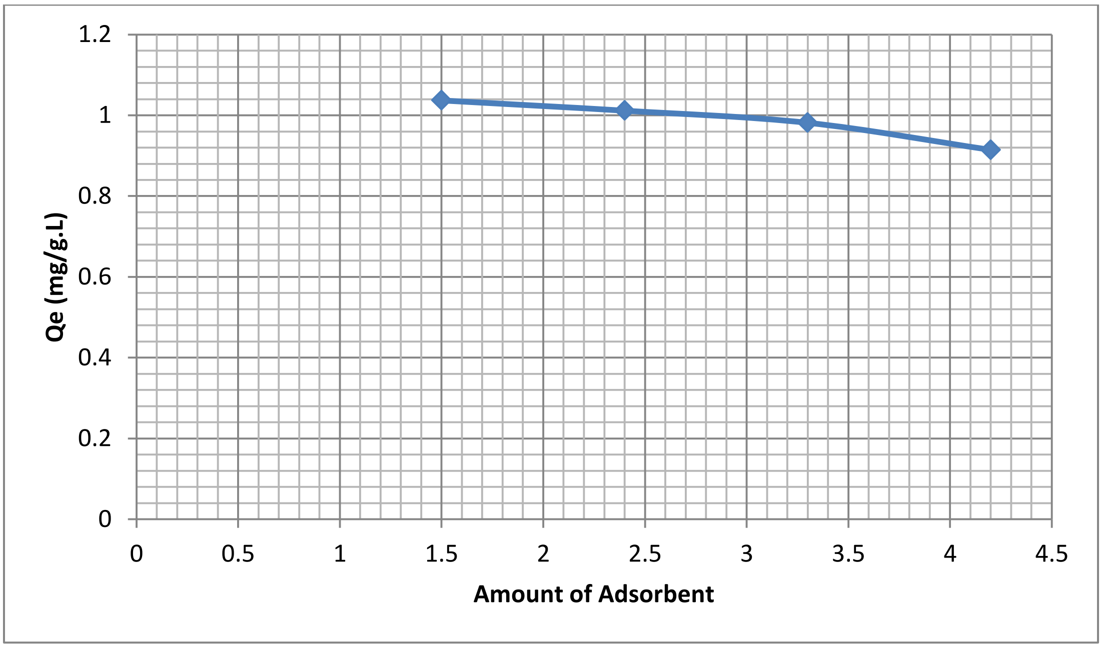

Figure 4-11 Amount of Adsorbent vs Efficiency at 10 mg/L solution

Based on the results gained from part 4.1, part 4.2 and part 4.3 we can see that the efficiency is actually increases as the concentration of the fluoride itself increases. However it is need to be noted that despite the high efficiency, the concentration rarely drops to the needed concentration which is below 1.5 mg/L in one step of adsorption.

4.4 Testing the Regeneration Capability

Based on Logathanan et al (2012) weak acids are often chosen as a method to regenerates used adsorbent. However in the same article also said that mostly calcium based adsorbent also regenerated using hydroxide ions. The solution prepared was distilled water with the addition of 0.01 mol of NaOH, Acetic Acid, and Phosporic acid which were put on different beaker. A solution of pure distilled water as a reference. The final concentration of fluoride after several hours of treatment is tested on the Ion Chromatograph to see the amount of fluoride released by the used eggshell under different treatments.

Originally, the experiment was conducted using sodium hydroxide, phosphoric acid and acetic acid. However only solution that was treated with hydroxide and distilled water that shows the amount of fluoride in the solution after regeneration process. The solutions treated with acetic acid and phosphoric acid was unable to be detected by Ion Chromatograph device. One of the reasons is the reaction happening between fluoride and the acids. For example the reaction of fluoride and the phosphoric acid which binds the fluoride and calcium to make the compound fluoroapatite, thus makes it unable to be detected by the Ion Chromatography device. The result gained from the experiment is shown on the table and figure below:

Table 4-7 Final Fluoride Concentration

Experiment	Eggshell Amount (g)	Final Concentration (mg/l)					
		0 hours	2 hours	6 hours	24 hours	30 hours	48 hours
Distilled Water	1.5	0.004	0.048	0.184	1.131	1.131	1.097
OH	1.5	0.005	0.047	0.098	0.131	0.209	0.201

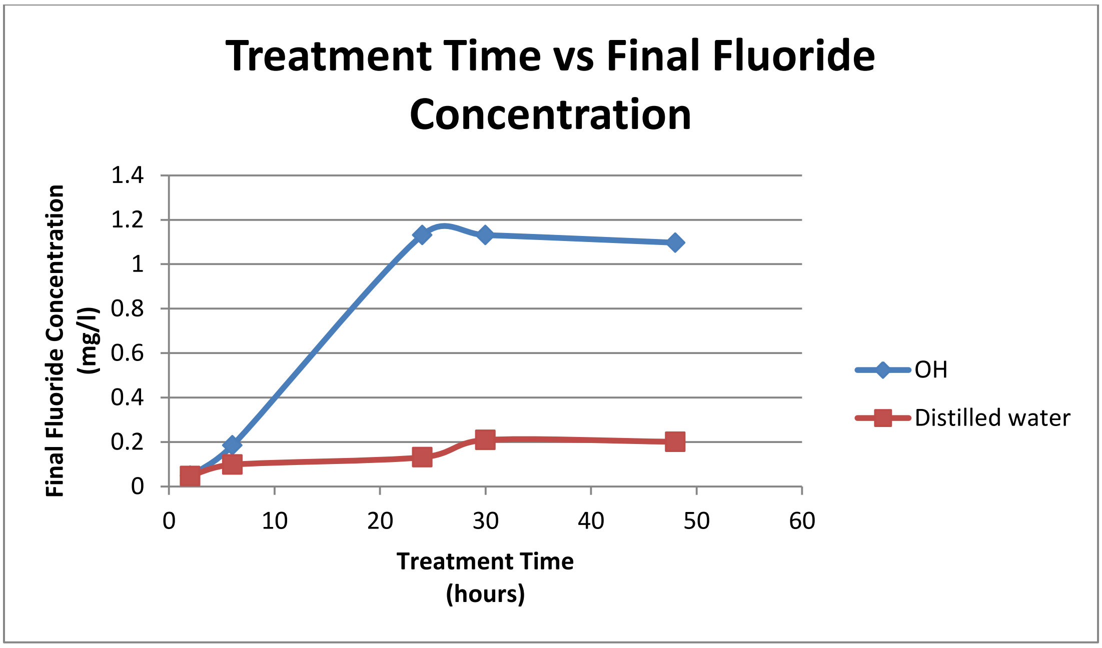

Figure 4-12 Treatment Time vs Final Fluoride Concentration

From the experiment it's clearly seen that the concentration increases significantly, which signals the release of fluoride ion into the water. The solution which is treated with sodium hydroxide shows a higher concentration in the final concentration of fluoride compared with distilled water only. Therefore it shows that the hydroxide ion is capable in assisting the regeneration of calcium based fluoride adsorbent as proposed by Loghatanan et al (2012).

Based on the previous experiment of testing the effect of pH and amount of adsorbent, it is found that the overall absorbed amount of fluoride reaches 4.5547 mg where the total amount of eggshell used was 45.6 grams. Therefore we get the average amount of adsorbent fluoride in the eggshell per gram of eggshell is

$$Adsorbed\ fluoride = \frac{4.5547}{45.6} = 0.099\ \frac{mg\ fluoride}{g\ eggshell}$$

Thus the efficiency of the regeneration is

$$efficiency = \frac{((1.131\frac{mg}{L})/(0.1L))}{1.5\ g\ X\ 0.1044\frac{mg}{g}} X100\% = 75.49\ \%$$

The amount of the efficiency is taken at the highest point where it results in a good efficiency of 72.23%. It is also to be noted that at 48 hours the concentration slightly dropped, where this might shows the timing where the fluoride is actually begin to be adsorbed by the eggshell again. Therefore it is advised not to perform the regeneration more than 30 hours.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

Adsorption is one of the widely used and cheap methods of removal of fluoride where its adsorption efficiency and its cost depend on the type of adsorbent used. The adsorbent used usually contains positive ions or cations that can attract the fluoride ions which are negatively charged. Eggshell is one of the candidates as an adsorbent of fluoride since it is mostly made of calcium, as well as it is a waste product thus it is cheap in price. Therefore a further study to analyze the effectiveness of the eggshell as fluoride adsorbent would be beneficial.

This study had proven that eggshell have a good potential as a fluoride adsorbent since it able to adsorb fluoride quite effectively. The optimum operating pH of the fluoride itself is maximized around pH 5 to pH 6 which can be easily maintained and can be easily converted back to drinkable pH after treatment of fluoride removal. The efficiency also increases as the concentration of the fluoride increases, however it is to be noted that the adsorption cannot reach to the safe amount in one time adsorption. Thus a further study in the number of stages needed to reach the safe level of below 1.5 ppm is further needed to be done. The study also manages to prove the ability of eggshell to be regenerated. However due to the cheapness of the eggshell and it can be easily replaced, a further study needed to be done to see which option is more feasible whether to replace it or to regenerate it.

5.2 Recommendation

There are several recommendations and suggestions that can be done in the future works. Fluoride standard solution should be used instead of using solid sodium fluoride in order to make it easier to control the solution concentration. A temperature control device such as hot plate can also be used to maintain temperature or test the effect of temperature as well as stirring using magnetic stirrer instead of using jar test. Using mechanical grinder to make fine particles of eggshell can also be done to further increase adsorption capacity of the eggshell. A further study can be done in order to see the effect of time or flow on the adsorption thus making it possible to design the actual adsorption chamber. Finally an economic study regarding which is more feasible whether to regenerate or replace used adsorbent can also be done.

REFFERENCES

[1] Fawell,J., Bailey, K., Chilton, E., Dahi, E., Fewtrell, L., Magara, Y., Fluoride in Drinking Water, World Health Organization, IWA Publishing, UK, 2006.

[2] World Health Organisation, Guidelines for Drinking-water Quality, Volume 2. *Health Criteria and Other Supporting Information, second ed.*, World Health Organisation, Geneva, 1996.

[3] Unicef Position on Dental Fluorosis. (n.d.). Retrieved from http://www.nofluoride.com/Unicef_fluor.cfm

[4] Logathanan, P., Vigneswaran, S., Kasandamy, J., & Naidu, R. (2012). Defluoridation of drinking water using adsorption processes. *Journal of Hazardous Material*,

[5] Gupta, V.K., Carrott, J.M., Carrott, M.M.L.R. Suhas, Low-cost adsorbents: Growing approach to wastewater treatment – a review. *Crit. Rev. Environ. Sci. Technol.* 39 (2009) 783–842.

[6] Teng, S., Wang,, Gong, W., Liu, X., Gao, B., Removal of fluoride by hydrous manganese oxide-coated alumina: performance and mechanism. *J. Hazard. Mater.* 168 (2009) 1004–1011.

[7] Weiner, E.R., Applications of Environmental Aquatic Chemistry, CRC Press, Taylor and Francis Group, Florida, 2008.

[8] Sivasamy, A., Singh, K.P., Mohan, D., Maruthamuthu, M., Studies on defluoridation of water by coal-based sorbents. *J. Chem. Technol. Biotechnol*. 76 (2001) 717–722.

[9] Tokunaga, S., Haron, S.A., Wasay, S.A., Wong, K.F., Laosangthum, K. Uchiumi, A., Removal of fluoride ions from aqueous solutions by multivalent metal compounds. *Inter. J. Environ. Studies* 48 (1995) 17–28.

[10] Meenakshi, S., Viswanathan, N., Identification of selective ion-exchange resin for fluoride sorption. *J. Colloid Interface Sci*. 308 (2007) 438–450.

[11] Onyango, M.S., Kojima, Y., Aoyi, O., Bernardo, E.C., Matsuda, H., Adsorption equilibrium modelling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. *J. Coloid Interface Sci.* 279 (2004) 341–350.

[12] Lv, L., He, J., Wei, M., Evans, D.G., Duan, X., Factors influencing the removal of fluo-ride from aqueous solution by calcined Mg-Al-CO3 layered double hydroxides. *J. Hazard. Mater*. B133 (2006) 119–128.

[13] Ruixia, L., Jinlong, G., Hongxiao, T., Adsorption of fluoride, phosphate, and arsenate ions on a new type of ion exchange fiber. *J. Colloid Interface Sci.* 248 (2002) 268–274.

[14] A.H. Parsons, Structure of the eggshell, Poult. Sci. 61 (1982) 2013–2021.

[15] Nakano, T., Ikawa, N.I., Ozimek, L., Chemical composition of chicken eggshell and shell membranes, *Poult. Sci*. 82 (2003) 510–514.

[16] Bhaumik, R., Mondal, K., Das, B., Roy, P., Pal, K. C., Das, C., Banerjee, A., & Datta, J. K. (2012). Eggshell powder as an adsorbent for removal of fluoride from aqueous solution : equilibrium kinetic and thermodynamic studies.

[17] Fluoride in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality. World Health Organization, 2004

[18] Environmental Health Criteria 227: Fluorides. World Health Organization, 2002, p. 38

[19] Whitford, G.,M. (1994). Intake and Metabolism of Fluoride. *Advances in Dental Research*

[20] Yeung, C.,A. (2008). A systematic review of the efficacy and safety of fluoridation. *Evid Based Den*