FLUORIDE ION REMOVAL USING COFFEE GROUNDS BASED ADSORBENT

KHOO TIONG HENG

A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering

Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature :

Name : Khoo Tiong Heng

ID No. : 1500559

Date : 18/9/2018

APPROVAL FOR SUBMISSION

I certify that this project report entitled **“FLUORIDE ION REMOVAL USING COFFEE GROUNDS BASED ADSORBENT”** was prepared by **KHOO TIONG HENG** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : ______________________

Supervisor : Dr. Lai Soon Onn

Date : 18/9/2018

Signature : ______________________

Co-Supervisor : ______________________

Date : ______________________

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ABSTRACT

Fluoride removal on wastewater is currently a key research due to the rapid development on semiconductor manufacturing and metal processing industry. This study performed several batch adsorption tests to determine the removal efficiency and adsorption capacity of fluoride on spent coffee grounds based adsorbent (SCGA). The spent coffee grounds (SCG) was subjected to chemical modification with HCl acid solution and followed by carbonisation process at temperature of 700 ℃. SCGA was characterised using Scanning Electron Microscope (SEM), Energy-dispersive X-ray Spectroscope (EDX) and Fourier Transform Infrared Spectrometer (FTIR). For the parameter test, the maximum fluoride uptake was obtained at initial fluoride concentration of 100 mg/L, 30 mins of contact time, 0.6 g of adsorbent dosage and initial pH 6 of wastewater. A maximum fluoride removal efficiency of 67% could be achieved using SCGA as an adsorbent. The experimental data on adsorption capacity was best described by Langmuir Isotherm. From the kinetics perspective, the fluoride adsorption obeyed the pseudo-second-order kinetic model. Overall, the SCGA has a great potential to serve as an economic and efficient adsorbent for fluoride removal in industrial wastewater.

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ABBREVIATIONS

Ce	Equilibrium fluoride concentration, mg/L
Ci	Initial fluoride concentration, mg/L
Q_e	Adsorption capacity at equilibrium, mg/g
Q_t	Adsorption capacity at time t, mg/g
Q_m	Equilibrium capacity for complete monolayer adsorption, mg/g
K_L	Langmuir constant
K_F	Freundlich constant
n_f	Adsorption intensity constant
R_F	Separation factor
k_1	Pseudo-first-order rate constant
k_2	Pseudo-second-order rate constant
V	Volume of the fluoride solution (L)
m	Mass of adsorbent (g)
COD	Chemical oxygen demand
BOD	Biological oxygen demand
SCGA	Spent coffee ground adsorbent
PZC	Point of zero charge

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Water pollution due to increasing industrial activity has become a global issue of concern. The excessive concentration of toxic substances in water effluent including the fluoride has caused severe environmental effect and is also detrimental to human health. For the excessive intake of fluoride by human being, it will lead to fluorosis. In fact, fluorosis causes the embrittlement of teeth, bones and even causes neurological damage in some severe cases (Fan, Parker and Smith, 2003).

Fluoride exists naturally as an ion in the groundwater with concentrations ranging between 0 and 41 mg/L (Vithanage and Bhattacharya, 2015). In Ethiopia, fluoride in groundwater can achieve a high concentration of 205 mg/L (National Research Council, 2006). Recently, the countries including India, China and countries in Southeast Asia have been found to have high concentrations of fluoride existing in groundwater (Mohapatra et al., 2009). Many countries in Africa are significantly affected by the fluorosis problem due to the limited resources and development fluoride removal technologies.

Based on the studies conducted, high fluoride contamination in the world was mainly contributed by the industrial wastewaters. Fluoride forms a common aqueous effluent in many chemical industries. The wastewater effluent from the semiconductor manufacturing, aluminium smelters, electroplating, ceramic production contains high fluoride concentrations. In fact, hydrofluoric acid solutions applied in metal processing industry mainly contribute to the fluoride effluent into the wastewater generated. The effluent needs proper treatment to reduce fluoride concentration to an acceptable limit before discharging into the public sewage.

Currently, there are several commonly applied pollutants removal techniques on industrial wastewaters include membrane filtration, chemical precipitation, ion-exchange and adsorption method (Fu and Wang, 2011). In fact, adsorption technique is widely applied in wastewater treatment due to the low cost, high effectiveness on various pollutants and availability of adsorbents. There are several adsorbents have been utilised in industry for pollutants removal including activated alumina, zeolites and lastly activated carbon (Bhatnagar and Sillanpää, 2010).

However, the cost for the implementation of adsorption technique is relatively high compared to other removal methods. Hence, the recent studies have been shifted by researchers to investigate an effective, low cost and environmental friendly material for adsorption technology.

1.2 Importance of The Study

This research is important as the adsorption performance of SCG based adsorbent was determined. The SCG is utilised to remove excessive fluoride ions contained in the wastewater. It has been an interest of researchers to discover a new adsorbent which is low cost, effective and highly available. Future research can be conducted using this operating parameter for industrial application on large-scale fluoride wastewater treatment.

The technology also can be implemented in the developing countries which lack of resources and has limitation on implementing the high cost operation such as ion exchange, membrane filtration and reverse osmosis techniques for fluoride removal.

1.3 Problem Statement

Nowadays, fluoride contamination is a major issue worldwide. The drinking water and wastewater contamination are caused by the natural and anthropogenic activities which significantly affects the human health and also causes environmental impact (Bhatnagar et al., 2011).

The countries in North America, Africa and Asia have noticed a high fluoride concentration in groundwater (Mohapatra et al., 2009). Hence, it is crucial to decrease the fluoride concentrations to an acceptable limit. Finding a suitable technology for the efficient removal of fluoride from wastewater is a currently a main concern.

Besides, a cost-effective method is needed for the fluoride removal in the industrial application. Adsorption process is considered as a defluorination technique which can be considered in terms of performance, cost and also the design and operation.

1.4 Aim and Objectives

The ultimate aim of this study was to remove fluoride ions from synthetic wastewater to an acceptable level using spent coffee grounds based adsorbent (SCGA). In order to achieve the aim of this study, there were several objectives to be accomplished:

i. To investigate the surface characteristics of SCG, acid treated SCG, SCGA before and after the adsorption of fluoride.
ii. To evaluate the fluoride removal efficiency and adsorption capacity of SCGA by performing batch adsorption.
iii. To identify the optimum conditions for the adsorption process in terms of initial fluoride concentration, contact time, adsorbent dosage and pH of the solution.
iv. To obtain the adsorption isotherm model to describe the mechanism of fluoride adsorption.
v. To determine the adsorption kinetic model for SCGA.

1.5 Scope of the Study

In this study, spent coffee grounds based adsorbent has been chosen to remove fluoride ions from the synthetic fluoride solution. The following scope has been proposed to achieve the objectives of this research.

i. Prepare the synthetic fluoride solution and fabricate the adsorbent using chemical reagent for the modification process.
ii. Characterise the adsorbent in terms of the surface morphology, elementary information and functional groups.
iii. Investigate the effects of initial fluoride concentration, contact time, adsorbent dosage and pH of solution in the experiment.
iv. Analyse the results using the adsorption isotherm models including Langmuir and Freundlich Isotherm and kinetic models such as pseudo-first-order and pseudo-second-order.

1.6 Contribution of the Study

Throughout this study, the SCG pre-treatment conditions and the optimum parameters for fluoride removal using SCGA can be used for reference in the future research carried out. The findings and methodology for the experiment can be further improved for better adsorption efficiency.

1.7 Outline of the Report

There are five main chapters for this report including general introduction, literature review, methodology and work plan, results and discussion and lastly the conclusion and recommendation part. The basic principal and knowledge on this research topic can be obtained in the literature review part. By utilizing the findings and conclusion made by the researcher, a suitable methodology for the fabrication of adsorbent using spent coffee grounds can be developed. After performing the experiment, results obtained are further discussed and analysed. A final conclusion was made and some recommendations for improvements.

CHAPTER 2

LITERATURE REVIEW

2.1 General Introduction to Fluoride Ion

Fluoride is essential for human health. In fact, the optimal fluoride concentration for drinking water between 0.5 and 1 mg/L has to be maintained. As the concentration of fluoride is higher than the safety limit, it will cause a disorder known as fluorosis. As the fluoride enters the human body, about 75-90% of fluoride will be adsorbed (Fawell, 2006). After fluoride enters the blood stream, it will be distributed throughout the body. It has a tendency to accumulate in calcium rich areas such as teeth and bones (Fawell, 2006). The fluoride intake is mainly from the water, food and dental products consumed.

Excessive fluoride intake causes dental, skeletal fluorosis, and even leads to disruption of growth and neurological damage. According to the World Health Organization (WHO), the maximum acceptable fluoride concentration of drinking water is 1.5 mg/L (WHO, 2004). There are also regulations set for the industrial wastewater discharge limit for toxic substances stated in Environmental Quality Act 1974 (2017). The maximum fluoride concentrations are 2 and 5 mg/L for the Standards A and B, respectively. Standard A refers to the discharge into any inland waters within catchment areas, while Standard B refers to any other inland waters or Malaysian waters.

In fact, fluoride is used in many industrial processes such as aluminium manufacturing, steel processing, and semiconductor parts cleaning. The effluents contain high concentration of fluoride are released into the nearby water bodies. Hence, the removal of excess fluoride ion in the wastewater is important for the consideration on environmental impact and human health.

2.1.1 Sources of Effluent Containing Fluoride

There are basically two types of fluoride containing effluent which they are produced naturally or through industrial effluents. The dissolution of minerals and eruption of volcanoes can lead to emission of fluoride into surrounding atmosphere or water bodies. Besides, industrial activities also produce waste, process water and combustion gases which contain high concentration of fluoride. The wastewater discharged from the industry contains high fluoride concentrations ranging from 10 to 1000 mg/L. Table 2.1 presents the sources of fluoride effluent and the corresponding fluoride concentration and pH of the wastewater.

Table 2.1: Fluoride Concentration and pH in Different Industrial Effluent

Type of Industry	**Fluoride Concentration in Wastewater (mg/L)**	**pH of wastewater**
Semiconductor Manufacturing	83	6.38
	217	2.18
	350 - 1000	3.5
Aluminium Processing	80 - 90	-
Steel Manufacturing	5-35	7
	40-65	8.8 – 9.3
Photovoltaic Energy Manufacturer	217	2.18

Industries which are responsible for the fluoride containing effluent are the semiconductor manufacturing, coal combustion, production of glass and ceramic, electroplating and aluminium smelters (Shen et al., 2003). Besides, the usage of fluoride-containing pesticides also contributes to the emission of fluoride. Based on studies conducted, the aluminium manufacture as well as the phosphate ore industry have the most fluoride emission into the environment (Tjandraatmadja et al., 2010).

There are several anthropogenic sources for the fluoride emission. First of all, the hydrofluoric acid is widely used in the semiconductor industry, chemicals, solvents and plastics production. Another emission is noticed from the sulphur hexafluoride which is widely used in variety of electronic components and involved in production of aluminium and magnesium. Calcium fluoride is also considered one of the sources of emission which is widely used in glass and aluminium manufacturing (Inchem, n.d.).

2.1.2 Fluoride Removal Techniques

For the treatment of wastewater with excessive fluoride concentration, several technologies have been introduced. Basically, the methods include chemical precipitation, membrane filtration, electro dialysis, ion-exchange and the adsorption method.

Throughout the fluoride removal methods, membrane filtration, ion exchange and electro-dialysis are considered effective and able to lower the fluoride concentration to a desired level. However, the following methods are expensive and also frequent regeneration is required. For instance, the regeneration is needed for ion exchange resin and cleaning of membrane due to fouling. Table 2.2 shows the comparison made on the interest and limitations for different fluoride removal technique.

Among the various methods introduced for the fluoride removal in the water and also industrial wastewater, the adsorption method is widely utilized and applied. The main reason for choosing adsorption is that it provides satisfactory results in the removal efficiency. In fact, adsorption technique for fluoride removal was chosen for this study in terms of cost, efficiency, simplicity of design and operation (Mohapatra et al., 2009).

Table 2.2**:** Comparison of the Interest and Limitations on Different Fluoride Removal Technique (S. Waghmare & Arfin, 2015)

Removal Technique	Interest	Limitation
Precipitation and Coagulation	• Generally applied technique. • Practical and easy to understand.	• Required chemical dosages are high. • Sludge transfer issue.
Reverse Osmosis (RO)	• Fluoride removal of more than 90% regardless of initial concentration. • Applicable on wide pH range. • Not influenced by the presence of other ions.	• High Operating Cost. • Valuable minerals are removed. • Water becomes acidic after treatment and pH improvement is needed.
Nano Filtration Membrane	• High productivity. • No chemicals needed. • Not interfered with the presence of other ions.	• High operating cost. • Prone to fouling, scaling or membrane degradation.
Electro Dialysis	• Less chemical required. • High water recovery.	• Only applicable on separation of ionic components. • Huge power consumption.

Removal Technique	Interest	Limitation
Ion Exchange Process	• High efficiency can be achieved. • (90-95% fluoride removal)	• High in cost. • Treated water contains high concentration of chloride and pH value is low. • Interference due to the presence of other anions. • Problem on regeneration of resin.
Adsorption	• Ease of operation. • High efficiency on fluoride removal (up to 90%).	• High concentration of total dissolved solids causes fouling. • Drop in removal effectiveness after every regeneration. • Presence of other anions may interfere and compete on the actives sites on adsorbent.

2.2 Adsorption Technique

2.2.1 Definition and Mechanism

Adsorption refers to the phenomenon of which the accumulation of one substance on the surface of other substance in a solution (Adsorption, 2009). The initiation of adsorption is mainly due to the existence of unstable forces in the solution or surface of solid substances. These physical or chemical forces have a tendency to attract the substances nearby and interact with the absorbents surface.

However, adsorption is a term which is totally different from the absorption. In general, absorption is defined as the dispersion of substance throughout the bulk. Sorption process is known as both of the adsorption and adsorption processes occurs simultaneously.

In the adsorption system, both adsorbent and adsorbate are involved in the solution. Adsorbent will have the tendency to attract adsorbate in the bulk solution. The adsorption performance will depend on many factors including surface charge, presence of functional groups and solution pH. The mechanism of adsorption is illustrated in Figure 2.1.

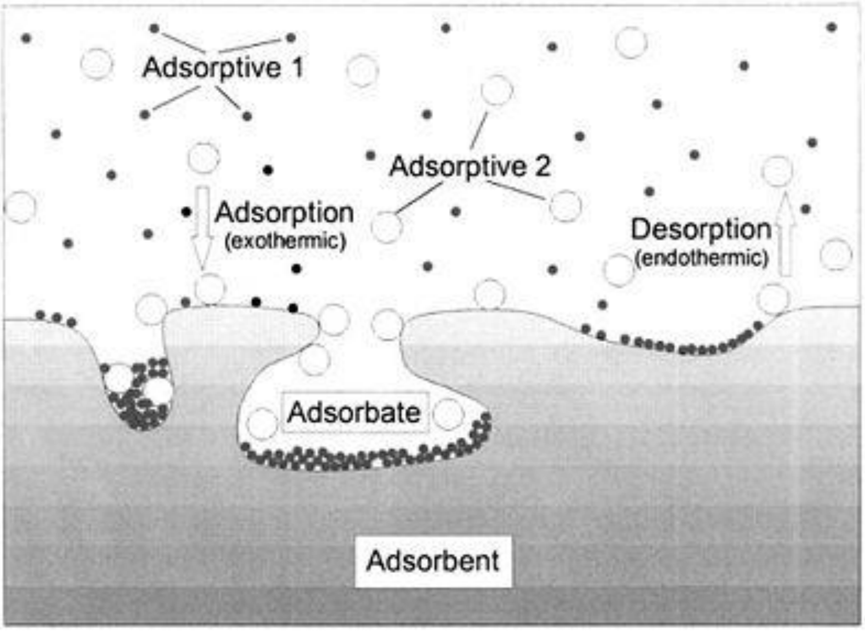


Figure 2.1: Mechanism of Adsorption Process

2.2.2 Types of Adsorption

Based on the forces which attract the adsorbate on the surface of adsorbent, they are separated into two types of adsorption which is the physisorption and chemisorption.

For the physisorption, the molecules of adsorbate are normally held on the surface of adsorbent by Van der Waals forces or weak physical forces. An example for this type of adsorption is the accumulation of ammonia gas on the surface of activated charcoal (Surface Chemistry, 2017). The adsorption type which the attraction of adsorbate with the surface of the adsorbent by chemical forces (chemical bonds) is known as the chemisorption. For instance, the accumulation of oxygen on the surface of tungsten is one of the chemical adsorption (Surface Chemistry, 2017). Table 2.3 summarise the characteristics of both physisorption and chemisorption process.

Table 2.3: Comparison on Characteristics of Both Types of Adsorption
(Adsorption, 2009)

Physisorption	**Chemisorption**
Dominated by Van der Waal’s forces	Attracted by chemical bond forces
Preferable at low temperature condition	Favourable at high temperature condition
Low energy required for adsorption (20-40 kJ/mol).	High energy required for adsorption (40-400 kJ/mol).
Process is reversible	Process is irreversible
No activation energy is needed	Activation energy is required for the process
Forms multi-molecular layers	Forms mono-molecular layers

2.2.3 Factors Affecting Adsorption Performance

The adsorption capacity of fluoride ion in the solution is influenced by several factors including pH, co-existing ions and adsorbent particle size.

The most important factor which influences the overall adsorption performance is the pH of solution. By manipulating the pH, the degree of the ionization of adsorbate and the adsorbent surface charge will be influenced. Besides, the activity of various functional groups on the active sites of adsorbent will be affected by pH of solution.

Based on the studies conducted by Loganathan et al. (2013), fluoride adsorption was relatively weak at extremely high and low pH. The maximum adsorption capacity could be achieved at optimal pH of solution within 4 to 8. According to Liao and Shi. (2005), as the pH value lower than 4, the reduction in fluoride adsorption was encountered due to the formation of hydrofluoride (HF) formed. At pH lower than 3, HF has low affinity towards the adsorbent. While in the pH above 7, the concentrations of hydroxyl, bicarbonate and silicates ions increase and compete with fluoride for adsorption. In addition, the surface becomes negatively charged in high pH of solution.

The point of zero charge (PZC) also affects the degree of fluoride adsorption. For instance, the PZC of Fe and Al oxides is ranged from 7 to 8 and maximum amount of fluoride is removed at pH 6–8 (Kumar et al., 2009). On the other hand, adsorbent with a PZC of 3.9–4.7 can achieve a maximum fluoride removal at pH 3–4 (Ramos et al., 1999).

It can be concluded that removal of fluoride is generally lowest at extreme high and low pH values. In the natural water which is neutral in pH, the adsorption capacity is the highest. Hence, for effective fluoride treatment process, the prior pH adjustment is not required if the wastewater is relatively neutral.

2.3 Activated Carbon (AC)

Activated carbon is a carbonaceous material which has a highly porous structure and a huge internal surface area. It plays an important role as a water purification media, pollutant gas adsorbent and also catalyst support (Cermakova et al., 2017). In the past, AC is fabricated using coals, wood and peat. However, the raw material used are considered non-renewable resources and also high in cost. Hence, the recent studies focus on using the agriculture residues or waste as the raw material for the production of AC. The raw materials include coconut shell, nut shell and rice husk which are abundantly available and low cost. By implementing this method, it will be an alternative for the adsorbent and also contributes to the reduction of residue waste which causes environmental impact (Mazlan et al., 2016).

However, for the removal of anionic contaminants, AC has poor adsorption capacity due to its low PZC (pH 1.6–3.5). Hence, surface modifications such as chemical and physical modifications can be applied to further improve the adsorption capacity.

2.4 Spent Coffee Grounds (SCG)

SCG is known as one of the low-cost adsorbents which is suitable for removal of metal ion and also fluoride ion.

2.4.1 Introduction

Nowadays, coffee is known as one of the most common types of beverages consumed worldwide. In fact, it is the second largest commodity after petroleum with a world production of around 8 million tons (Brienzo et al., 2016). The coffee annual consumption in Portugal was around 43,000 tons in 2011, which is a huge amount of consumption documented. There are millions metric tons of waste generated each year as a result of coffee production processes (Summers et al., 2014). The caffeine contain in the residues can lead to several environment impacts. Besides, a high chemical (COD) and biology oxygen demand (BOD) are discovered in the liquid effluent from manufacture of coffee. Hence, an oxygenation process is required before disposed into the environment (Brienzo et al., 2016). The solid wastes generated are usually combusted, ensilaged, or serves as a natural fertilizer.

During the coffee brewing process, a large quantity of waste is produced, which mainly consists of spent coffee grounds (SCG), which refers to used coffee grounds. In the instant coffee and beverage production, there are primary coffee waste of 45% generated as the by-product (Murthy, et al., 2012). In the coffee beverage preparation, raw coffee powder is in contact with hot water or steam to release the aroma compounds and other substances in the coffee beans. After the processes, a high moisture content of SCG (80-85%) will be produced with the characteristics of fine particle size, high organic load and acidic in nature (Mussatto et al., 2011). Figure 2.2 illustrates the SEM image of both roasted coffee beans and spent coffee ground.

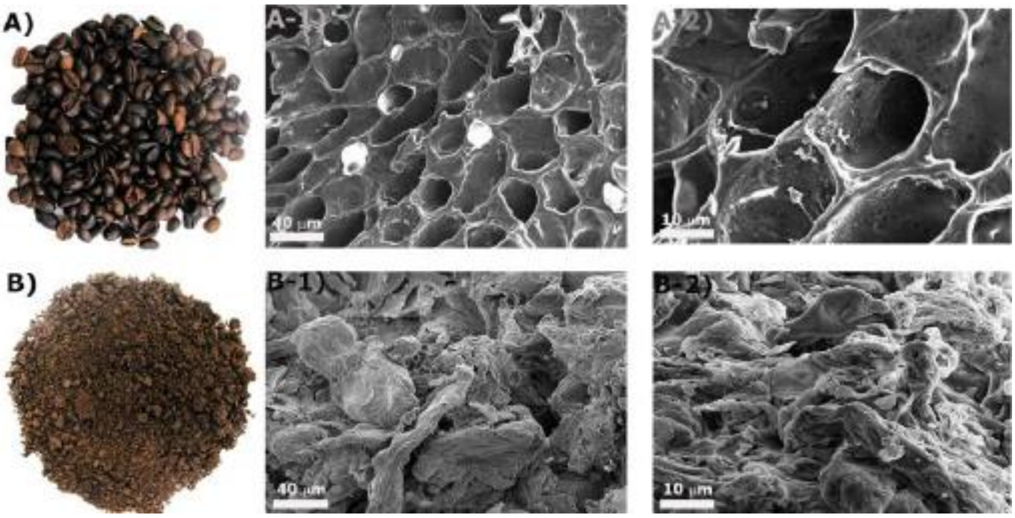


Figure 2.2: The Scanning Electron Microscope (SEM) Images of Roasted Coffee Beans (A) and Spent Coffee Grounds (B)

2.4.2 Applications of Spent Coffee Grounds (SCG)

SCG is a valuable source of natural antioxidants by the phenolic compounds recovery. The antioxidants produced can be utilised in health care, pharmaceutical production and also nutrition supplements (Zuorro and Lavecchia, 2012). In fact, phenolic has several advantages on human health including the prevention of chronic degenerative diseases, cardiovascular diseases and cancer. Panusa et al. (2013) stated that the antioxidant activity of SCG was mainly contributed by the presence of phenolic compounds.

Based on a study, extracts from SCG exhibited anti-tumor and anti-allergic properties, which are mainly due to the presence of phenolic compounds such as chlorogenic acid in the extracts. In general, the main components of interest in SCG are chlorogenic acids, caffeine and caffeic acid. The quantity of different substances in SCG is dependent on the coffee production process (Mussatto et al., 2011).

Caffeine is recognized to promote energy metabolism, while chlorogenic acids are can be used to prevent diabetes and some types of cancer. In addition, caffeic acid, as a constituent of antioxidant has exhibited the antimutagenic, antibacterial and anticarcinogenic properties. Therefore, it is definitely a best alternative to obtain the antioxidant compounds by extracting phenolic compounds from SCG, a low-cost material and available in large quantity (Mussatto et al., 2011).

SCG can be utilised for the biodiesel production which is an alternative and renewable energy source. Extraction of oil from SCG is a great concern due to the increased interest in biodiesel as an environmentally-friendly fuel. Based on the research conducted, crude lipids extracted from the SCG were converted into fatty acid methyl ester (FAME) and fatty acid ethyl ester (FAEE) via the non-catalytic biodiesel transesterification reaction. However, the direct conversion of bioethanol from SCG was not found to be a desirable option, due to relatively slow enzymatic behaviour in the presence of triglycerides and the free fatty acids (FFAs) exist in the raw materials.

The potential of SCG as feedstock for ethanol production is due its carbohydrates content such as cellulose and hemicellulose. The SCG also contains from 7 to 20% (dry bases) of lipids with reduced content by comparing with the fresh coffee bean. As a result, these oils will be more suitable for biodiesel production compared with fresh coffee beans, resulting in a higher quality biodiesel (Evans, 2014). However, the oil extraction from SCG at large scale requires technical improvement.

Besides, the use of SCG as a low-cost adsorbent for the biosorption of heavy metals from aqueous solutions has also been investigated, showing high efficiency for the removal of Cd, Cr(II) and Cr(IV), Cu and Pb. Also, the generation of biochar (pyrolysis) from SCG and its use for heavy metal removal was investigated. The adsorption performance for Zn, Cd, Cu and Zn are satisfying and hence the SCG can be utilised as a bio-adsorbent.

2.5 Preparation of Spent Coffee Ground Based Adsorbent

There are several factors influence the adsorption capacity, which includes the surface area, pore diameter, porosity and the surface functional group of the adsorbent. In general, the performance of adsorption rises with the surface area of adsorbent which closely relates to the number of active sites. This study focuses on the affinity of certain contaminants in wastewater and the modification procedures made to enhance the adsorption capacity of adsorbent. Basically, the modification can be categorized in two classes, which are chemical and physical modification.

2.5.1 Chemical Modification

Basically, the chemical reagent used are sulphuric acid (H_2SO_4), $ZnCl_2$, H_3PO_4, and hydrochloric acid (HCl), KOH, K_2CO_3 and NaOH (Ahmadpour and Do, 1996). In fact, the chemical modification involves carbonisation of the precursor with the presence of chemical reagents. The impregnation ratio of chemical agent to the adsorbent has a significant impact on the pore size distribution and the pore volume. According to Kalderis et al. (2008) and Koren et al. (2013), by subjecting to higher impregnation ratio, the adsorbent fabricated has larger pore capacity and larger surface. Besides, Kalderis et al. (2008) has proven that the usage of $ZnCI_2$ as an activating agent, the hydrogen and oxygen atoms of the raw material has been removed as water, lead to the formation of pores and further enhance the carbon content of adsorbent.

There are several advantages of using chemical modification in the fabrication process. First of all, the reaction temperature used is lower compared to the physical modification process, thus result in better pore structure on the adsorbent fabricated (Kwiatkowski and Broniek, 2017). Due to the lower reaction temperature, hence lower energy is required for the modification process and result in reduced cost. In addition, it provides more easier control on the pore structure development of adsorbent and also reduce the tar formation during the heating process. However, modification of carbon using chemical agent also has downsides such as requirement of extra rinsing procedure to remove the residue or excessive chemical after the carbonisation step. Nowadays, the combination of chemical and physical modification is widely applied in industrial adsorbent manufacturing.

Lopez-Ramon et al. (2001) has concluded that the adsorbent produced with chemical modification of olive-mill wastewater using KOH has higher surface area and porosity compared to the physical modification with carbon dioxide at 840 ℃. In short, chemical modification method is preferred over physical modification in terms of better porous structure development and enhance the adsorption capacity of adsorbent fabricated.

2.5.2 Physical Modification

In general, physical modification involves two stages which are the carbonisation and followed by the modification process. At the initial stage, the precursor material is pyrolyzed in an inert atmosphere at lower temperature (300-800 ℃). However, after the initial stage, low adsorption capacity is observed due to the tars condense on the adsorbent surface and causes blockage on pores. Hence, the following step is required which is the modification process at higher temperature (700-1000 ℃) with the presence of activating agents such as steam and carbon dioxide (Pallarés, González and Arauzo, 2018). In fact, carbon dioxide is preferred over the steam due to lower reactivity at high temperature conditions. In addition, carbon dioxide enhances the development of micro pores compared to steam as it favours the meso and macropore formation (Molina et al, 1996).

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

This chapter discussed the preparation of spent coffee grounds based adsorbent (SCGA) including material preparation, chemical modification and carbonisation process. The equipment, such as scanning electron microscope (SEM), Energy-dispersive X-ray (EDX) and Fourier Transform Infrared Spectrometer (FTIR) used for SCGA characterisation was described. Next, experimental procedures on parameter test (initial fluoride concentration, contact time, adsorbent dosage, pH) were further discussed and lastly the adsorption isotherms and kinetic models were introduced to describe the mechanism of fluoride adsorption.

3.2 Preparation of Spent Coffee Grounds Based Adsorbent (SCGA)

3.2.1 Pre-treatment of SCG

The spent coffee grounds (SCG) was provided by the "Amitie" café located in Bandar Sungai Long, Kajang, Selangor. First of all, the spent coffee grounds (SCG) collected were washed with certain amount of distilled water to remove dust and any water-soluble substances such as coloured component. It was subsequently dried in an oven for 8 h at a temperature of 105 °C. After drying, SCG was sieved to a uniform particle size of 300 μm using the "Prada" Test Sieve. Lastly, sieved SCG were stored in an airtight container to prevent the moulding due to the presence of moisture in the air.

3.2.2 Preparation of Hydrochloric Acid (HCl)

The activating agent chosen for this study was the hydrochloric acid (HCl) to modify the surface properties of SCG. Hence, for preparation of 0.1 and 0.5 M of HCl solution (500 mL), 4.17 and 20.84 mL of concentrated HCl were used respectively. First of all, the volumetric flask was filled with distilled water before adding the acid (HCl). Micropipette was used during the addition of acid into distilled water and the flask was well-shaken to homogenise the solution. The prepared acid solution was poured into a Scott bottle for storage purpose. However, the acid must be used in 2-3 days to prevent the degradation of acid and affected the accuracy of results.

3.2.3 Chemical Modification of Spent Coffee Grounds Adsorbent

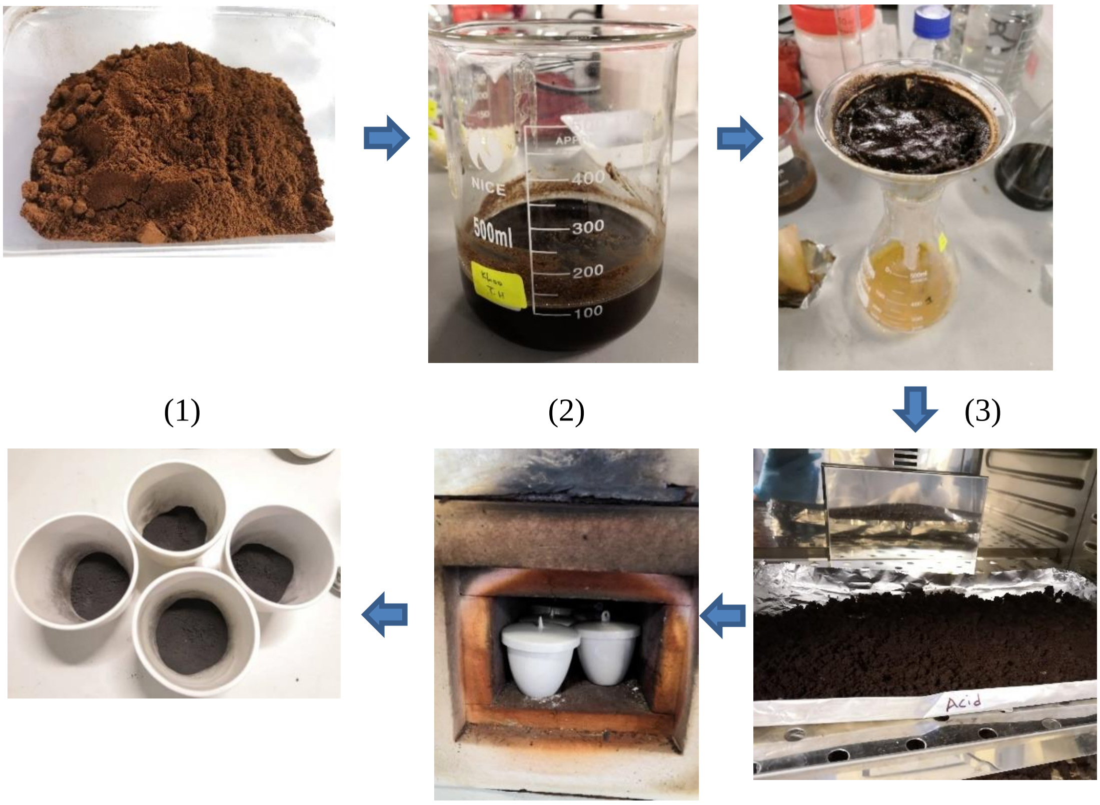
SCG was immersed in the prepared HCl solution in the beaker with the ratio of 1:3 (SCG: Acid solution) for 24 h. During the period, the solution was stirred regularly to ensure the adsorbent was fully immersed into the solution for efficient chemical treatment. After the treatment, the adsorbent was dried in an oven for 8 h at a temperature of 105 °C.

3.2.4 Carbonisation Process

After the chemical modification step, the adsorbent treated with different concentration of acid was carbonised at 700 °C for 1, 1.5 and 2 h, respectively. It was aimed to eliminate the volatile compounds. The process consisted of 3 stages include heating, holding and cooling in a programmable furnace. There was a constant heating rate of 10 °C / min for the carbonisation process.

The overall procedures of SCGA preparation were fully demonstrated in Figure 3.2 and the fabricated SCGA was presented in Figure 3.1.

Figure 3.1: Sample of Prepared Spent Coffee Grounds Adsorbent (SCGA)



(1) (2) (3)

(6) (5) (4)

Figure 3.2: Overall Process of SCGA Preparation. (1) Raw SCG; (2) Acid Treatment (3) Filter out Acid; (4) Drying in oven; (5) Carbonisation Process; (6) SCGA

3.3 Preparation of Synthetic Wastewater

Fluoride stock solution of 1000 mg/L was prepared using the sodium fluoride (NaF) salt. A total of 1 g sodium fluoride salt was needed for preparation of 1 L synthetic fluoride wastewater. Distilled water was used for the dilution of the stock solution during the batch adsorption test.

3.4 Characterisation of Adsorbent

In order to study the adsorption mechanism and the suitability of SCGA as an efficient adsorbent of fluoride, several analyses were carried out to determine the surface morphology, elemental composition and surface functional groups of SCG, acid treated SCG, SCGA before and after the fluoride adsorption.

3.4.1 Surface Morphology and Elemental Analysis

The surface morphology of SCG, acid treated SCG, SCGA before and after adsorption were determined by examining the porous structure using the Hitachi S-3400N Scanning Electron Microscope (SEM) (Figure 3.3). In order to perform the analysis, the powdered adsorbents were prepared on the sample holder (Figure 3.4). A layer of electrically conductive adhesive was applied to ensure the electrical flow to the sample on the holder. For the scanning purpose, the adsorbents were coated by a layer of gold film (electric-conducting material) (Figure 3.5).

Besides, the analysis on chemical composition of adsorbent in weight and atomic percentage was performed using Energy Dispersive X-ray spectroscope (EDX) incorporated with SEM equipment (Figure 3.3). For the operating principal, the elemental composition of the adsorbent is determined by detecting the X-rays created from the incident electrons of SEM. The elementary information was obtained for SCG before and after acid treatment to study the effectiveness of acid treatment.

Figure 3.3: Scanning Electron Microscope (S-3400 N, Hitachi) Incorporated with EDX

Figure 3.4: Powdered SCGA Prepared on Sample Holder

Figure 3.5: Coating of Electric-conducting Material (Gold Film)

3.4.2 Fourier Transform Infrared Spectrometer Analysis (FTIR)

Fourier transform analysis is a useful instrument which determines the existence of surface functional groups which interact with the fluoride ions. In this study, the Nicolet Brand of FTIR instrument (Model: IS10) was used to identify the functional groups on SCG, SCGA before and after the adsorption process.

3.5 Experimental Setup

Adsorption experiment was conducted using 250 mL conical flasks and an orbital shaker. The shaker was operated using a constant speed of 150 rpm at room temperature with the conical flasks placed on it. Different amounts of SCGA were added into the 100 mL of synthesis fluoride solution with the initial concentration ranging from 100 to 500 mg/L. The effect of pH of solution and the contact time on the adsorption efficiency and capacity were also studied. After the adsorption, adsorbent was filtered out using filter paper and the final fluoride concentration was measured using the UV-Vis spectrophotometer (Model: DR 3900, HACH).

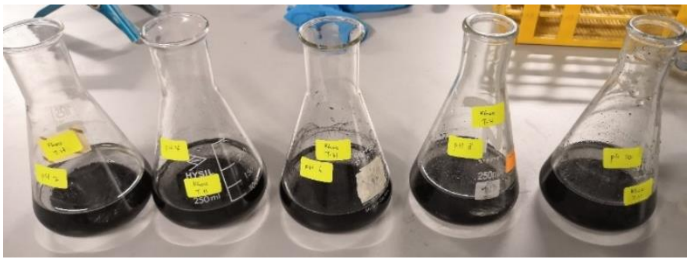


Figure 3.6: Batch Adsorption Test on Fluoride Removal

3.5.1 Initial Fluoride Ion Concentration and Contact Time

The synthetic fluoride solutions with initial concentration of 100, 300 and 500 mg/L, were prepared by diluting the stock solution (1000 mg/L). The range of concentration was determined based on the commercial fluoride wastewater concentration ranging from 50 to 1000 mg/L.

The adsorption efficiency and capacity of SCGA were determined in the time intervals of 10, 20, 30, 40 and 50 mins with different initial fluoride concentrations. A sufficient contact time was needed to achieve the equilibrium of adsorption.

3.5.2 Adsorbent Dosage

The amount of SCGA used in the fluoride removal was between 0.15 and 0.75 g with an increment of 0.15 g. A total of 5 different adsorbent dosages were used to determine the effects on fluoride removal percentage and adsorption capacity.

3.5.3 pH

pH plays an important role in fluoride removal as it will greatly influence on the surface charge to enhance the affinity of fluoride to the adsorbent. For this parameter study, solution pH was manipulated from pH 2 to 10 with an increment of 2. pH meter was used for the measurement of the solution pH, while hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to manipulate the pH.

3.6 Analysis of Adsorption Results

3.6.1 Percentage Removal and Adsorption Capacity

By using the data obtained in the batch fluoride adsorption test, the percentage of fluoride removal was computed using the Equation 3.1:

$$\text{Percentage removal} = \frac{C_i - C_e}{C_i} \times 100\% \tag{3.1}$$

where,

C_i = Initial fluoride concentration (mg/L)

C_e = Equilibrium fluoride concentration (mg/L)

The adsorption capacity of SCGA was determined from the following Equation 3.2:

$$Q_e = \frac{(C_i - C_e)V}{m} \tag{3.2}$$

where,

Q_e = Equilibrium adsorption capacity (mg/g)

V = volume of the fluoride solution (L)

m = mass of adsorbent (g).

3.6.2 Adsorption Isotherm

Adsorption isotherm is a study on the mechanism which involved the interaction of fluoride between the SCGA in the equilibrium state. In this research, the most commonly applied adsorption models, Langmuir and Freundlich Isotherm were applied to describe the fluoride adsorption at equilibrium state.

The Langmuir Isotherm (Equation 3.3) is applicable to the monolayer adsorption of fluoride on the adsorbent surface with finite number of identical active sites (Jeon, 2017). Besides, this model best represents the chemisorption which only allows only one molecule attached to the active sites, and hence no interaction between adsorbed molecules can be assumed. In short, at the saturation point, the adsorbent has a finite capacity and the adsorption system will approach equilibrium.

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3.3}$$

where,

Q_e = Equilibrium adsorption capacity (mg/g)

Q_m = equilibrium capacity for complete monolayer adsorption (mg/g)

K_L = Adsorption equilibrium constant (L/mg)

Freundlich Isotherm (Equation 3.4) is applicable on describing non-ideal adsorption on heterogeneous surfaces. The heterogeneity is mainly due to the presence of various surface functional groups and multiple interactions between adsorbates (Hameed and Khaiary, 2008).

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{3.4}$$

where,

K_F and *n* are Freundlich constants.

3.6.3 Adsorption Kinetic Models

By performing kinetics studies on fluoride adsorption, the adsorption process can be more efficient due to knowledge on the mechanism of adsorption and the rate limiting steps which affects the adsorption rate (Koay et al, 2016). The pseudo-first-order (Equation 3.5) and second order kinetic models (Equation 3.6) were used to examine the adsorption of fluoride by varying the contact time.

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \tag{3.5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{3.6}$$

where,

q_t = Equilibrium adsorption capacity (mg/g) at time *t* (min)

k_1 = Pseudo-first-order kinetic rate constant (min^{-1})

k_2 = Pseudo-second-order kinetic rate constant (min^{-1})

With the plot of $\log(q_e - q_t)$ against *t* and t/q_t against *t*, the rate constant k_1 and k_2 were computed through the slope of the curve and value of *y*-intercept, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

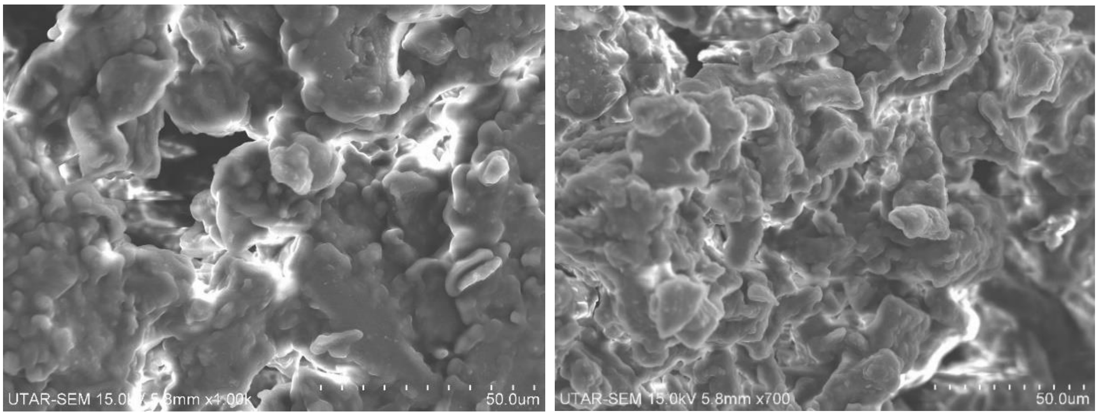
In this chapter, the results of batch adsorption parameter test, characterisation of spent coffee grounds based adsorbent (SCGA) using Scanning Electron Microscope/ Energy Dispersive X-ray (SEM/EDX) and Fourier Transform Infrared Spectrometer (FTIR) were discussed. The optimum pre-treatment conditions such as acid concentration and carbonisation time; operating parameters during batch adsorption test including initial fluoride concentration, contact time, adsorbent dosage and pH of solution were determined.

4.2 Characterisation of Spent Coffee Grounds (SCG) and Spent Coffee Grounds Based Adsorbent (SCGA)

For the characterisation of SCG and SCGA, the surface morphology, elementary information and functional groups were studied and observed using scanning electron microscope (SEM), Energy-dispersive X-ray (EDX), and Fourier Transform Infrared Spectrometer (FTIR), respectively.

4.2.1 Analysis of Scanning Electron Microscope (SEM)

In order to study the adsorption mechanism of fluoride onto SCGA, the following surface morphology was observed using scanning electron microscope (SEM). First of all, SEM images of raw SCG and acid (0.5 M HCl) treated SCG are shown in Figure 4.1. For raw SCG, it could be observed that the majority of the surfaces were fairly smooth with only several cracks. After being subjected to acid treatment, the surface of SCG was oxidised, and hence uneven surfaces and more cracks and layers were formed. The modification step was vital on increasing overall surface area of the SCG.

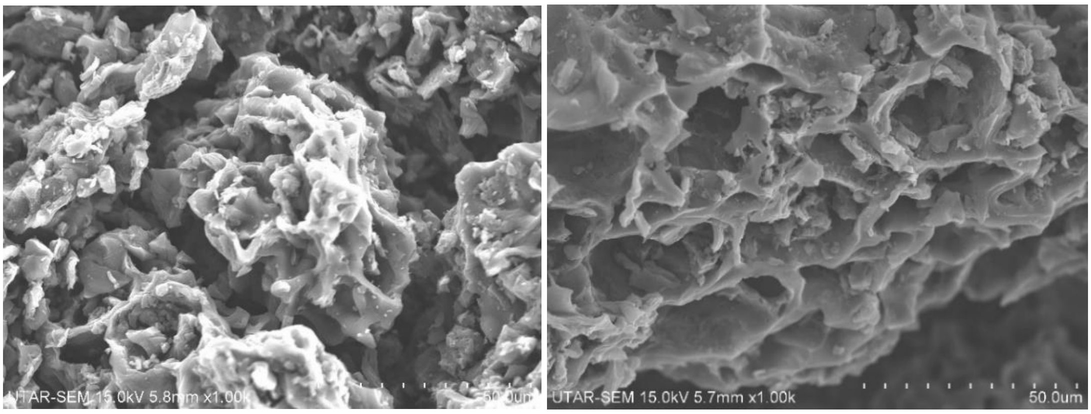


(A) (B)

Figure 4.1: Surface Morphology of SCG Before and After Chemical Modification with HCl. (A) Raw SCG (Magnification 1000 ×); (B) Acid Treated SCG (Magnification 700×)

After the chemical modification process, SCGA was fabricated through carbonisation process for 1 h at temperature of 700 °C. From the images shown in Figure 4.2, the porous structure was well-developed, with various pore sizes and shapes resulted from the carbonisation process. In fact, hydrochloric acid (HCl) act as a dehydrating agent and plays an important role in the carbonisation process. During the carbonisation, HCl will interact with the carbon surface and remove the substances as volatiles, and hence pores are formed (Chakrapani et al., 2010). The white pieces observed on the image might be the impurities on carbon surface.

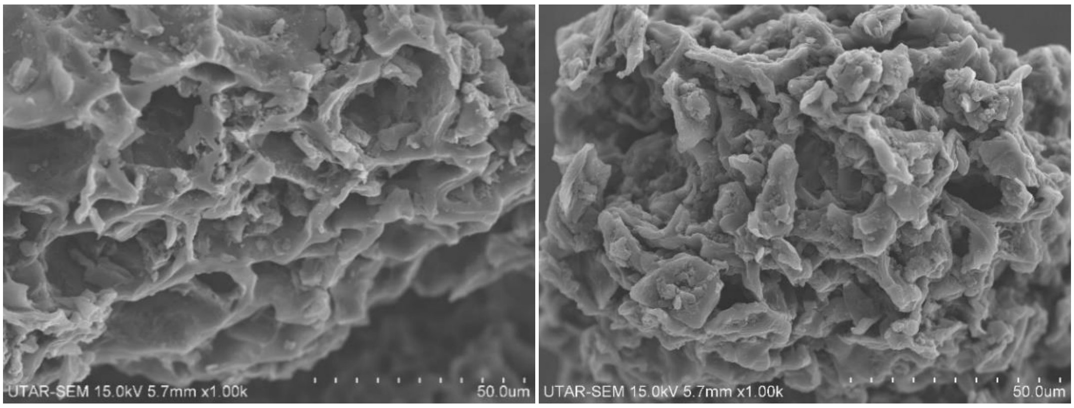
With different concentrations of acid treatment (0.1, and 0.5 M HCl), the surface morphology of prepared SCGA was different. Basically, by subjecting to higher concentration of acid (0.5 M), the SCGA possessed greater porosity and higher pore volume compared to those for acid concentration of 0.1 M. It allowed more fluoride ions to be accommodated in the pores of SCGA. Hence, 0.5 M acid treated SCGA presented higher adsorption efficiency compared to 0.1 M acid treated SCGA.



(C) (D)

Figure 4.2: Surface Morphology of SCGA Subjected to Different Acid Treatment (Magnification 1000×). (C) 0.1 M HCl (D) 0.5 M HCl

Figure 4.3 clearly shows the difference on surface of adsorbent before the batch adsorption test and after the adsorption process. Basically, after a contact time of 30 minutes, the adsorption achieved equilibrium which the fluoride ions were fully absorbed onto the adsorbent. As shown in Figure 4.3 (F), the pores were mostly filled and attached with adsorbate compared with the initial adsorbent.

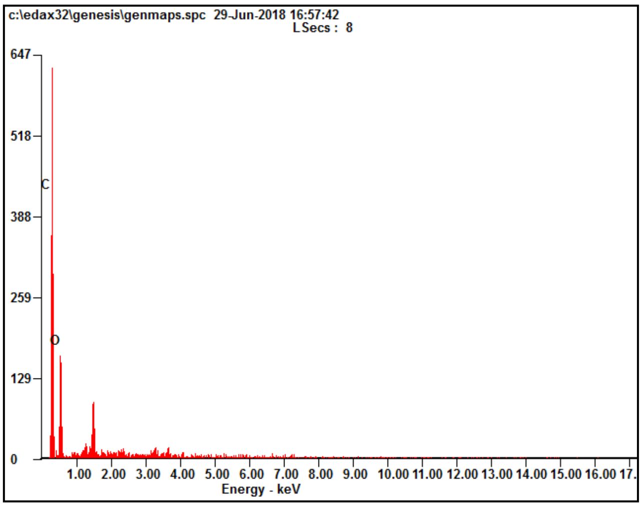


(E) (F)

Figure 4.3: Surface Morphology of SCGA for Fluoride Adsorption (Magnification 1000×). (E) Before Fluoride Adsorption (F) After Fluoride Adsorption

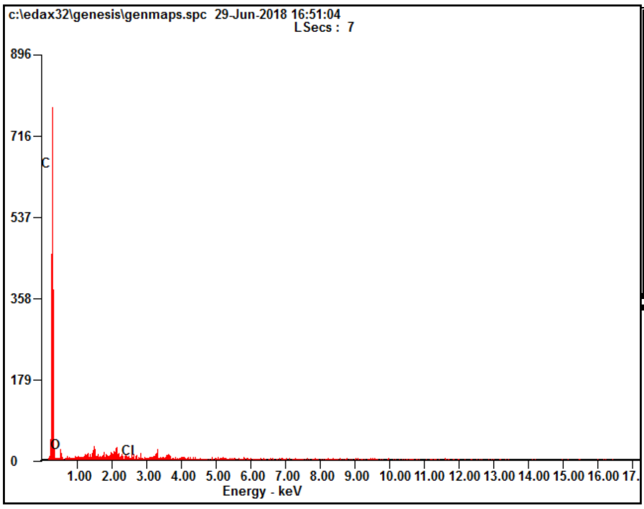
4.2.2 Analysis of Energy-dispersive X-ray Spectroscopy (EDX)

The surface compositions of spent coffee grounds and acid treated (0.5 M HCl) SCGA were illustrated in Figures 4.4 and 4.5, respectively. Spent coffee grounds is mainly composed of carbon (60.2 wt%) and oxygen (39.8 wt%). By referring to the results after chemical modification and carbonisation process, the SCGA mainly consisted of carbon and oxygen which were (91 wt% and 8 wt%, respectively. A relatively small amount of chloride (Cl) (1 wt%) was attached on the SCGA surface since hydrochloric acid was used as a modification agent. In short, the result highlighted that the oxygen was greatly reduced, and released during the carbonisation process which might contribute to the pore formation.



Element	***Wt%***	***At%***
CK	60.20	66.83
OK	39.80	33.17
Matrix	Correction	ZAF

Figure 4.4: EDX Elemental Signal and Composition of Raw Spent Coffee Grounds



Element	***Wt%***	***At%***
CK	90.91	93.39
OK	08.15	06.28
ClK	00.94	00.33
Matrix	Correction	ZAF

Figure 4.5: EDX Elemental Signal and Composition of 0.5 M Acid Treated SCGA

4.2.3 Analysis of Fourier Transform Infrared Spectrometer (FTIR)

In fact, surface functional groups have a significant impact on the adsorption mechanism and plays an important role in the ion removal efficiency. Hence, it is important to determine the functional groups present on the SCGA which enhances the fluoride adsorption. Table 4.1 summarise the surface functional groups of SCG, SCGA before and after fluoride adsorption which can be obtained from FTIR spectra in Appendix B.

For the raw SCG, there were several band presented at 3292, 2922, 2858, 1641, 1245, 1025, 875 cm^{-1} which were considered as the functional groups such as hydroxyls, olefins, esters and ethers (Largitte et al., 2016). However, after the carbonisation process, the spectrum of SCGA discovered that most of the functional groups present at precursor were lost during the heating process. It might be due to the chemical modification using hydrochloric acid solution on the SCG which deposited volatile compound on the carbon surface, leading to efficient surface modification. After the fluoride adsorption, there were several broad bands shifting from 2284, 2058 to 2180, 2064 cm^{-1} which might be attributed to the fluoride interactions between the surface functional groups. The band observed at 3245 cm^{-1} was due to the presence of O-H stretching bond.

Table 4.1: FTIR Analysis on Surface Functional Groups of SCG, SCGA Before and After Fluoride Adsorption

Reference	Wave Number (cm^{-1})			Functional Groups
	Raw SCG	SCGA	SCGA after F^- adsorption	
3600-3400	3292		3245	O-H Stretching of carboxylic
3000-2800	2922, 2858			C-H Stretching of alkane
2260-2100		2284, 2058	2180, 2064	C=C Stretching of alkyne
1650-1600	1641		1630	C=C Stretching of alkene
1300-1000	1245, 1025			C-O Stretching of ether and ester
1000-675	875			C=C-H Bending

4.3 Preparation of Spent Coffee Grounds Based Adsorbent

Before the commencement of batch adsorption test, raw spent coffee grounds (SCG) were prepared and subjected to different concentrations of acid treatment for chemical modification. Besides, the carbonisation time was also an important consideration as it would affect the adsorption capacity of the SCGA.

According to the summarised removal efficiency in Table 4.2, the fluoride removal percentage was shown based on the spent coffee grounds modification conditions with different amount of adsorbent used. During the chemical modification, 0.1 and 0.5 M of hydrochloric acid (HCl) were utilised as the oxidising agent to modify the surface of SCGs. The spent coffee grounds were also subjected to different carbonisation durations which were 1, 1.5 and 2 h, respectively.

Based on the results, the 0.5 M acid treated SCG was chosen as an efficient adsorbent in terms of percentage removal of fluoride. By comparing the adsorption efficiencies of 0.1 and 0.5 M acid treatment with 1 h of carbonisation time, it exhibited a 2 to 6% of increment in removal efficiency with same adsorbent dosage used. Higher concentration acid might produce more porous adsorbent with higher surface area to enhance the adsorption process. Besides, by increasing the carbonisation duration, the amount of fluoride adsorbed dropped. It may be due to the rupture of SCGA surface or more ash was produced at longer carbonisation time. According to Ayucitra et al. (2017), the spent coffee grounds carbonised at temperature of 400 °C and activated using 0.2 M HCl solution achieved a total removal percentage of 51.6 % for lead. The current research has demonstrated a better result in fluoride removal compared to previous researchers using spent coffee grounds as an adsorbent.

Table 4.2: Effect of Modification Conditions on Fluoride Removal Efficiency (%) with Different Adsorbent Dosages

Modification Specifications	**Adsorbent Dosage (g)**				
	0.15	**0.3**	**0.45**	**0.6**	**0.75**
0.1M HCl, 1 h carbonisation	52.8%	56.2%	57.2%	59.0%	56.8%
0.1M HCl, 1.5 h carbonisation	53.2%	55.6%	55.2%	55.2%	54.4%
0.1M HCl, 2 h carbonisation	52.4%	54.8%	55.8%	54.8%	56.2%
0.5M HCl, 1 h carbonisation	56.8%	58.6%	62.4%	64.2%	63.2%
0.5M HCl, 1.5 h carbonisation	55.2%	57.2%	60.8%	58.4%	59.8%
0.5M HCl, 2 h carbonisation	52.4%	55.8%	56.8%	55.2%	56.8%

4.4 Adsorption Parameter Study

Batch adsorption test was performed to study on fluoride removal in different parameters including initial fluoride concentration, contact time, adsorbent dosage and solution pH.

4.4.1 Effect of Initial Concentration of Synthetic Fluoride Wastewater and Contact Time

Based on Figure 4.6, the study was performed by manipulating the contact time from 10 to 50 min with different initial fluoride concentrations (100, 300, 500 mg/L). The adsorbent dosage used was 0.3 g with solution pH of 6 in this parameter study. Overall, it showed a significant increasing trend of fluoride removal for three initial fluoride concentrations from contact time of 10 to 20 min, while the curve increased slightly from 20 to 30 min. At contact time between 30 and 50 min, the adsorption removal approached equilibrium in which nearly linear curve was shown.

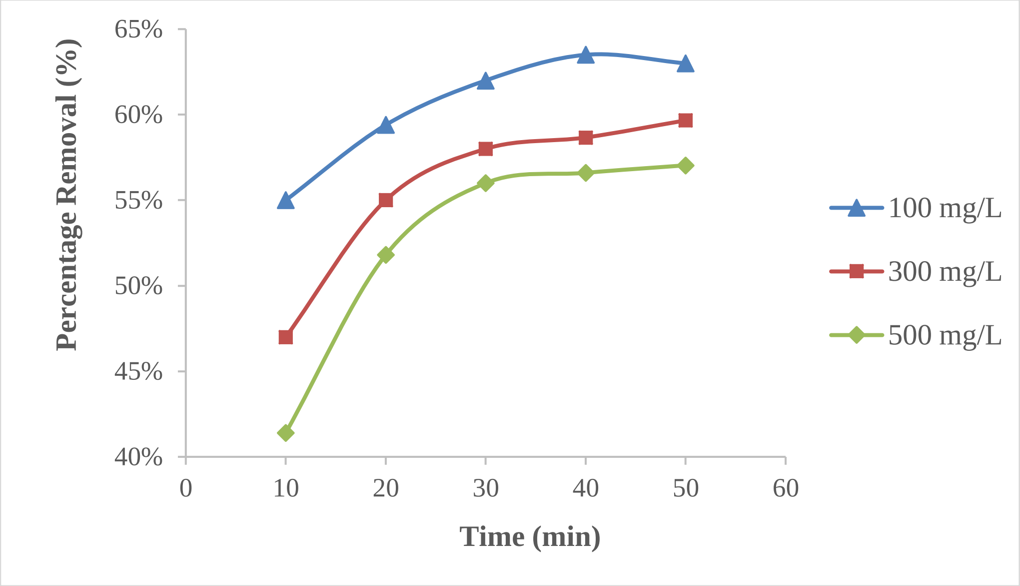


Figure 4.6: Effect of Contact Time on Removal Efficiency of Initial Concentration (100, 300, 500 mg/L)

In fact, at the initial stage of adsorption, the adsorbent active sites were free and open to interact with the fluoride ions. Hence, a high adsorption rate of adsorbent was observed at the initial stage. However, as the contact time increased, slower adsorption might be experienced due to lower rate of solute diffusion into the pores of the adsorbent (Chou et al., 2012). After a period of time, the active sites and pores were filled up by the fluoride ions, resulting in the saturation of active sites. The adsorption of adsorbent achieved equilibrium at time ranged from 40 to 50 min.

Besides, the effect of initial concentration had significant impact on the amount of fluoride ion removal. Based on the study conducted, the initial concentration with 100 mg/L had the highest removal efficiency, followed by the 300 mg/L and the 500 mg/L showed lowest percentage of fluoride removal. It was therefore deduced that higher the initial fluoride concentration, inhibited the adsorption of fluoride ions onto the SCGA surface. In fact, at lower initial fluoride concentration, the greater removal of fluoride was due to higher ratio of active sites on the adsorbent to the fluoride ions in the synthetic wastewater. It was also reported that the main causes of low removal efficiency might be attributed to lack of sufficient surface area to accommodate more fluoride ions in the synthetic solution. (Abdullah and Prasad 2009).

According to the results computed in Figure 4.6, at the contact time of 30 minutes, the removal efficiencies of fluoride ions were 62%, 58% and 56% for initial fluoride concentrations of 100, 300, 500 mg/L, respectively. This result showed that the solution with initial concentration of 100 and 300 mg/L had lower impact on the removal efficiency. As a comparison, Namane et al. (2005) found that by using coffee grounds based adsorbent for dye adsorption, the adsorption efficiency decreased from 85 to 65% as the initial dye concentration increased (20 to 70 mg/L). Besides, the percentage removal of dye also increased from 45 to 80 % when subjected to longer contact time (0 - 60 min). The similar trend was also obtained by other researchers. Besides, Getachew, Hussen and Rao (2015) determined the 80% of fluoride concentration could be removed within half an hour of time with 18 g of coffee husk based adsorbent. However, the initial fluoride concentration was relatively low (10 mg/L) and large amount of dosage was used compared to the current research.

In short, the lower initial fluoride concentration was preferable for adsorption and showed a higher fluoride removal efficiency. However, due to the relatively wide range of initial fluoride concentration of industrial wastewater (100 – 1000 mg/L), the study was conducted based on 500 mg/L of initial concentration for better illustration of result and study the application of spent coffee grounds based adsorbent in fluoride removal of highly polluted industrial wastewater.

Referring to Figure 4.7, the adsorption capacity significantly increased from 21 to 95 mg/g by increasing initial concentration from 100 to 500 mg/L. For initial fluoride solution of 500 mg/L, there was a significant change of adsorption capacity from 65 to 95 mg/g. In fact, the adsorption capacity was proportional to initial fluoride concentration which was different from the relationship of percentage removal with initial fluoride concentration.

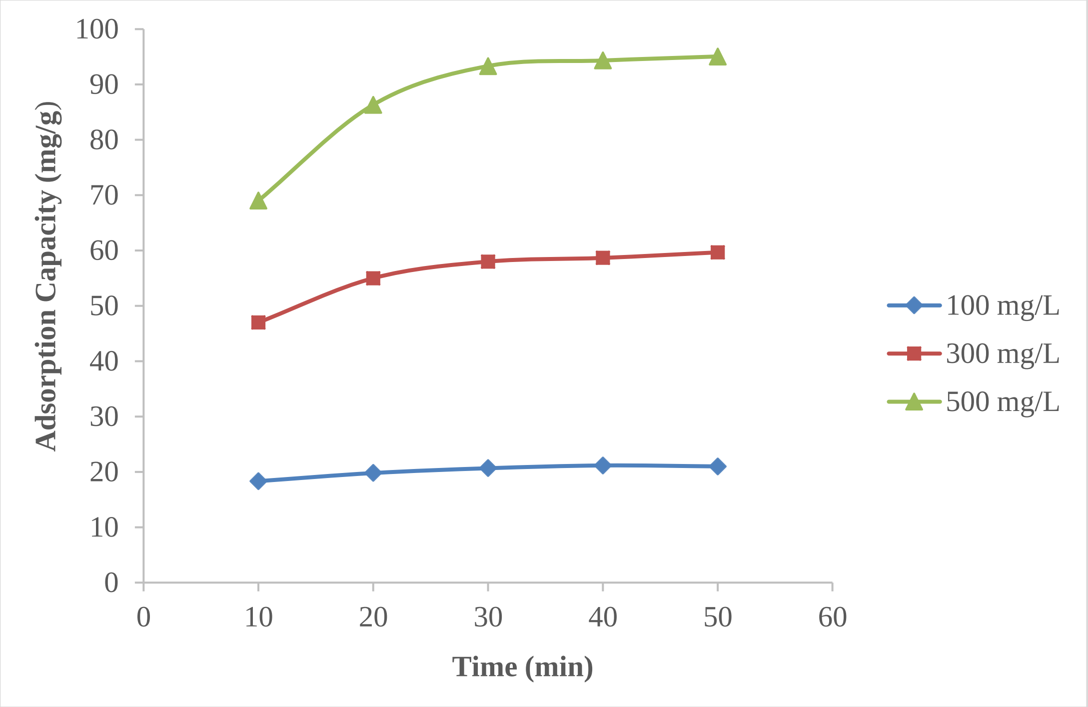


Figure 4.7: Effect of Contact Time on Adsorption Capacity of Different Initial Concentration (100, 300, 500 mg/L)

4.4.2 Effect of Adsorbent Dosage on Fluoride Adsorption

The amount of adsorbent utilised for the fluoride removal is one of the important parameters to determine the adsorption capacity with specified initial concentration. In this study, an initial fluoride concentration of 500 mg/L at pH of 6 with 30 mins contact time were selected as the adsorption conditions. Besides, the SCGA dosage was varied from 0.15 to 0.75 g with an increment of 0.15 g. Based on the removal efficiency results, the overall curve displayed an increasing trend from 57 to 62 % as the dosage of adsorbent increased from 0.15 to 0.75 g.

As the adsorption dosage increased from 0.15 to 0.45 g, the increment of fluoride removal efficiency was significant. This was mainly due to the increase of adsorption sites and surface area which were proportional to the amount of adsorbent. By further adding the SCGA, the adsorption was further enhanced in a slight increment. However, according to Figure 4.9, the amount of fluoride ions adsorbed per unit weight of adsorbent (Q_e) decreased from 189 to 41.6 mg/g as the SCGA was varied from 0.15 to 0.75 g. Since the adsorption capacity demonstrated a decreasing trend, a minimum value could be reached as the approached equilibrium which the adsorption sites were fully occupied and saturated. The similar trend was observed by Getachew, Hussen and Rao (2015) using coffee husk (arabica coffee) based adsrobent for fluoride removal.

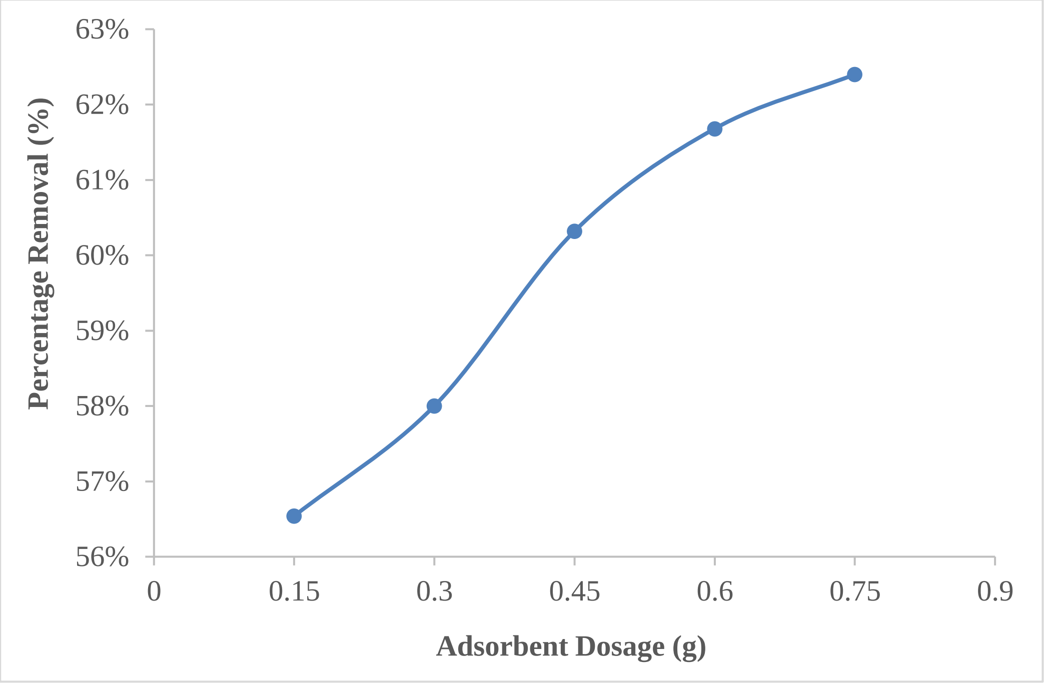


Figure 4.8: Effect of Adsorbent Dosage on Fluoride Removal Efficiency

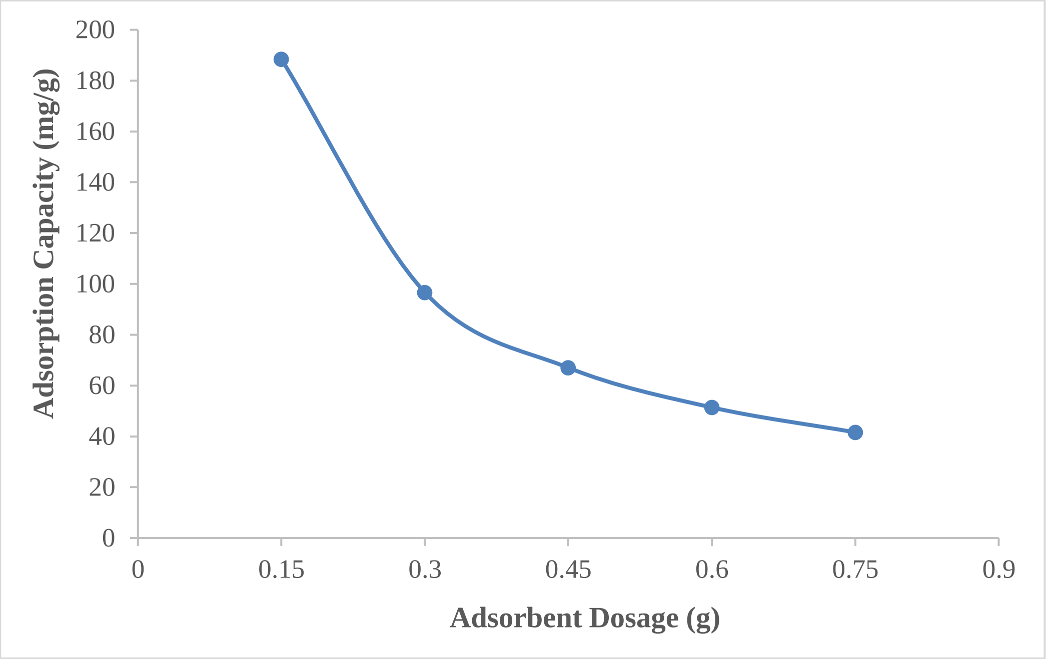


Figure 4.9: Effect of Adsorbent Dosage on Adsorption Capacity

4.4.3 pH

Removal of fluoride ions was found to be strongly dependent on the pH of the fluoride solution, which resulted in changes on adsorbent surface charge. In this parameter study, an amount of 0.6 g adsorbent was added into solution with pH ranging from 2 to 10. The initial fluoride concentration was constant for 5 sets of solution (500 mg/L) and subjected to contact time of 30 minutes.

Figure 4.10 shows the adsorption efficiency curve by varying solution pH. In the acid solution, the percentage removal increased from pH 2 to 4 and achieved maximum removal around pH 4-6. It remained nearly constant at neutral pH conditions. By further increasing the pH, the amount of fluoride removal gradually decreased from pH 6 and significantly dropped from pH 8 to 10. This finding proved that the adsorption of fluoride was preferred at acidic conditions over the alkaline condition. Besides, neutral pH (6-7) also exhibited good adsorption as compared to alkaline conditions.

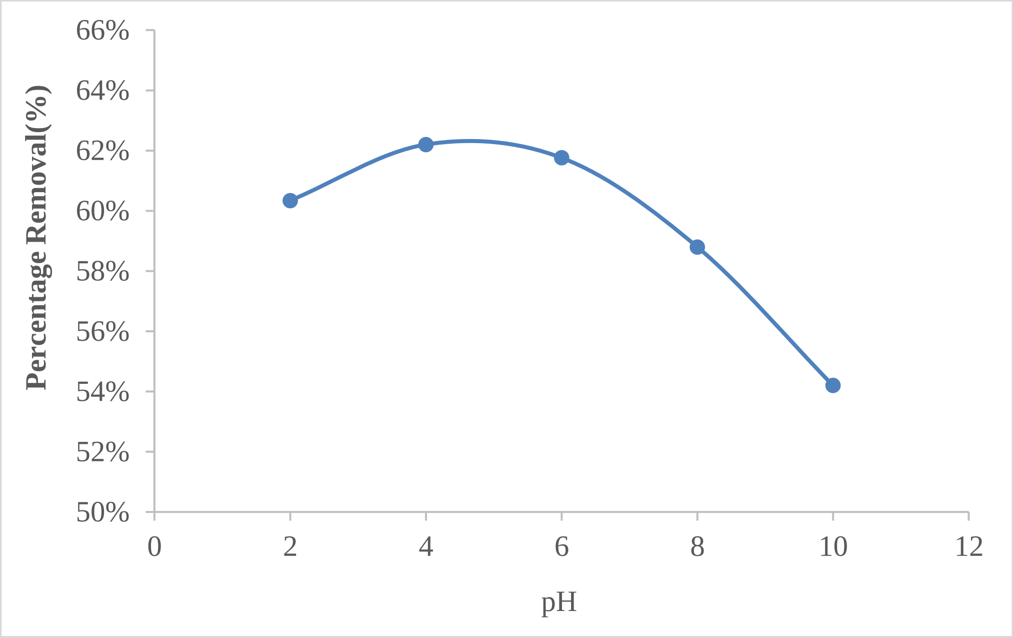


Figure 4.10: Effect of Solution pH on Percentage of Fluoride Removal

Hence, the results could be explained based on the point of zero charge (PZC). According to Kirby (2010), it is known as an indication of zero electrical charge on the surface of adsorbent. At pH below the PZC, the adsorbent surface become positively charged due to presence of H^+ ions, which facilitates the attraction of negatively charged ions (anion), i.e., fluoride ions in this study. Hence, the removal of fluoride ions and adsorption capacity were further enhanced when subjected to acidic solutions. However, at pH above the PZC of adsorbent, the repulsive effect occurred between fluoride in the solution and the negatively charged adsorbent surface. This interaction resulted in lower adsorption capacity. According to Wu et al. (2016), the zero point of charge of the spent coffee grounds carbon was determined to be 5.6. Likewise, the optimum pH for fluoride removal was at pH range of 4-6 in this study.

Based on the study of Getachew, Hussen and Rao (2015), the most optimum solution pH for fluoride removal was at pH of 2 using the coffee husk based adsorbent. However, this result was contrary to the principle on fluoride adsorption. According to the literature, at very low pH conditions, the fluoride ions will eventually be converted into hydrofluoride (HF). In fact, the affinity of hydrofluoride (HF) onto the carbon surface will be weaker in the solution pH which is less than 3 (Suneetha et al, 2015). Hence, lower adsorption efficiency was observed at extreme low pH condition (pH = 2).

According to Figure 4.11, as in the acidic and neutral conditions, the adsorbent exhibited high fluoride uptake capacity (100-104 mg/L), due to the positively charged and neutral active sites on the adsorbent surface. As the adsorbent was immersed in alkaline solution, the result of reduced adsorption capacity could be contributed by the competition of fluoride (F^-) and hydroxide ions (OH^-) in the solution for the available active sites on the adsorbent (Mourabet, 2012).

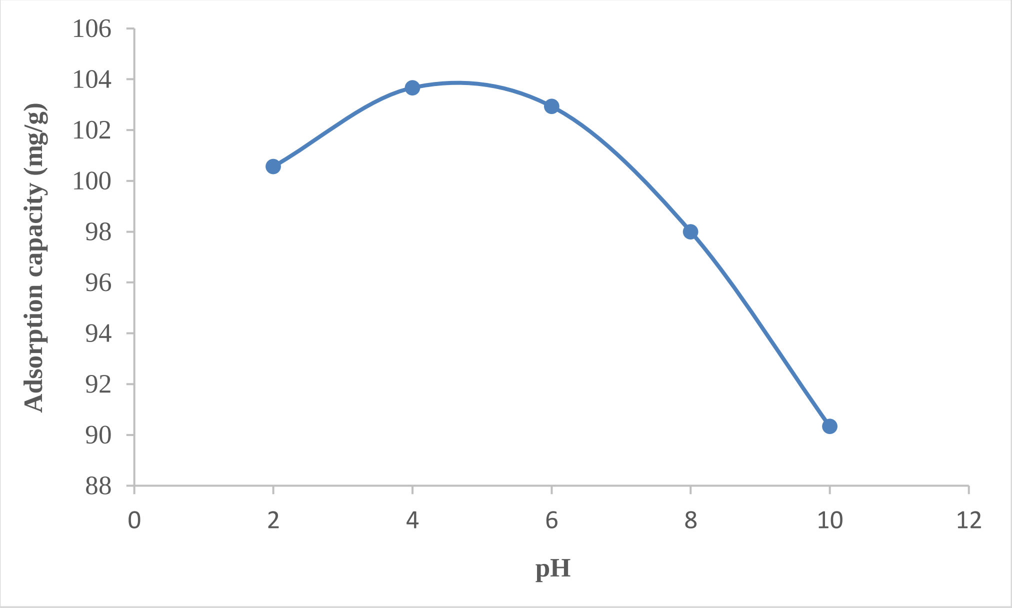


Figure 4.11: Effect of pH on Adsorption Capacity of SCGA

4.5 Adsorption Isotherms Models

In fact, adsorption isotherm is a useful technique to determine the mechanism of adsorption process, surface properties and the attraction of adsorbent towards the adsorbent used. For this study, Langmuir and Freundlich Isotherms were used to fully demonstrate the relationship between the fluoride ions remaining in the solution and amount of fluoride ions attached to the surface of adsorbent.

4.5.1 Langmuir Isotherm Model

By applying Langmuir Isotherm model, it assumes the uniform adsorption energies on the SCGA surface and no interaction between adsorbed fluorides. Besides, it represents the chemisorption which monolayer deposition is formed. In order to determine the applicability of the adsorption model, the following linear equation was applied to construct a curve.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \qquad (4.1)$$

where,

C_e = Equillibrium concentration of fluoride ion (mg/L)

Q_e = Equillibrium adsorption capacity (mg F^-/g adsorbent)

Q_m, K_L = Langmuir constant

According to Figure 4.12, the correlation coefficient (R^2) was determined to be 0.9851. Q_m and K_L are constants representing adsorption capacity and binding strength, respectively. Both of the Langmuir constants were obtained using the slope and intercept of the line plotted.

Calculation of Q_m and K_L:

$$\frac{1}{Q_m} = 0.0066$$

$$\boldsymbol{Q_m \quad = 151.52\ \mathrm{mg/g}}$$

$$\frac{1}{K_L Q_m} = 3.3286$$

$$\boldsymbol{K_L = 0.002}$$

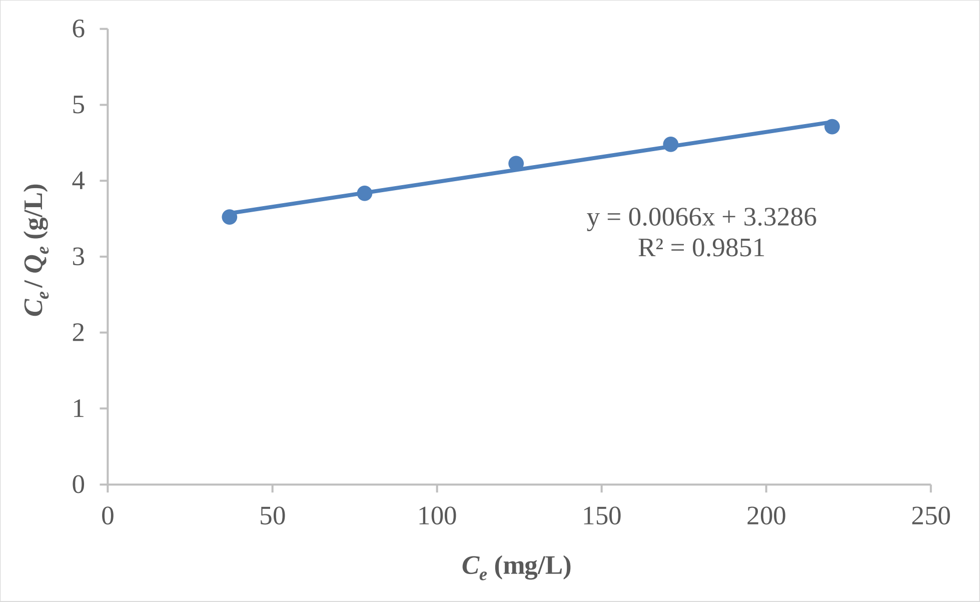


Figure 4.12: Langmuir Isotherm Plot for Fluoride Ion Removal

In order to determine the suitability for adsorption using the Langmuir isotherm model, separation factor was introduced. The values indicate the type of isotherm to be irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L = 1) or unfavourable (R_L > 1). Figure 4.13 clearly illustrates the calculated R_L against the initial fluoride concentration, C_i.

$$R_L = \frac{1}{(1+K_L C_i)} \tag{4.2}$$

where,

K_L = Langmuir constant

C_i = Initial fluoride concentration (mg/L)

The calculated separation factor R_L were 0.83 to 0.5 by increasing the initial fluoride concentration (Appendix B-5). Besides, the computed separation factor R_L ranged between 0 and 1, which indicated that the fluoride adsorption was favourable using the Langmuir Isotherm model.

4.5.2 Freundlich Isotherm Model

Apart from the Langmuir isotherm model, the adsorption of fluoride ions by the SCGA can also be described by Freundlich isotherm model which refers to surface heterogeneity of the adsorbent. The model assumes formation of multilayer adsorption which differs from the concept of Langmuir isotherm. Linear form of Freundlich equation can be expressed in Equation 4.3, where n and K_F are both Freundlich constants to describe adsorption intensity and adsorption capacity, respectively.

$$\log q_e = \frac{1}{n} logC_e + logK_F \tag{4.3}$$

Based on Figure 4.13, the graph was plotted with log Q_e (y-axis) against log C_e (x-axis). The slope and intercept determined from the straight line were 0.8346 and -0.2812, respectively. Hence, both of the constants were calculated based on the values obtained. Calculations were performed on computing Freundlich constants n and K_F:

$$n = \frac{1}{0.8346}$$
$$\boldsymbol{n = 1.2}$$

$$logK_F = -0.2812$$
$$\boldsymbol{K_F = 0.5234}$$

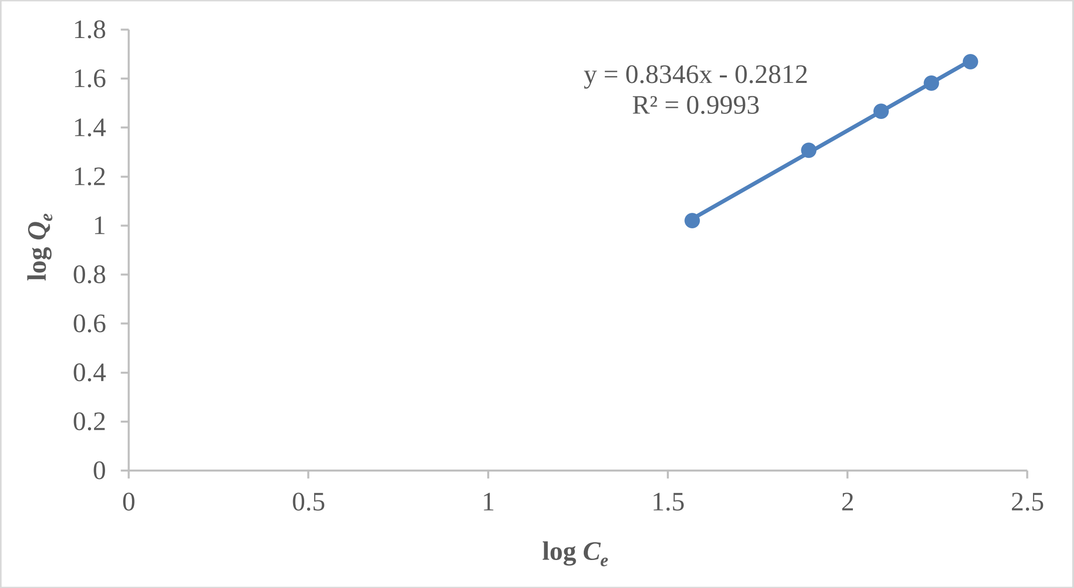


Figure 4.13: Freundlich Isotherm Plot for Fluoride Ion Removal

In fact, the magnitude of Freundlich constant, *n* provides an indication on the favourability of adsorption. In the range of 2–10, it is considered a good adsorption, while 1-2 is moderately difficult and poor adsorption occur at $n < 1$ (Treybal, 1981). As the calculated *n* value was between 1 and 2, it is considered as a moderately difficult adsorption.

Table 4.3 summarises the constants for respective isotherm models as well as the correlation coefficient, R^2. The correlation coefficient values for Langmuir and Freundlich isotherm models were 0.9851 and 0.9993, respectively, which indicated that the Freundlich isotherm model was slightly more compatible compared to the Langmuir isotherm model in describing the fluoride adsorption mechanism. However, due to the Freundlich constant, *n* which stated there was a difficult adsorption of fluoride ions, the Langmuir Isotherm was chosen as the most optimum model for adsorption mechanism description. In addition, both of the isotherm models had no significant difference in the correlation and possessed a relatively high value of correlation coefficient ($R^2 \approx 1$). The only limitation for Langmuir isotherm model is that it is only applicable under low pressure conditions. In short, the adsorption mechanism of fluoride adsorption was best represented by the chemisorption which monolayer deposition was formed on the surface of SCGA.

Table 4.3: Comparison on Correlation Factor and Constants for Langmuir and Freundlich Isotherm Models

	Langmuir Isotherm	**Freundlich Isotherm**
Isotherm constant, *K*	0.002	0.5234
Correlation Coefficient, R^2	0.9851	0.9993

4.6 Adsorption Kinetic Models

In order to study the mechanism of fluoride adsorption into the SCG based adsorbent, adsorption kinetics were used to determine the adsorption efficiency and investigate the reaction mechanism of adsorption process, such as mass transfer. The reaction kinetics can be represented by pseudo-first order or second order model.

4.6.1 Pseudo-first-order Kinetic Model

The pseudo-first-order kinetic model was plotted using the adsorption capacity data of 0.6 g adsorbent at pH of 6 with different contact times. Equation 4.4 expresses the linearized equation of pseudo-first-order kinetic, where k_1 is the rate constant and q (mg/g) is the adsorption capacity.

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \qquad (4.4)$$

Based on Figure 4.14, the slope and *y*-intercept were -0.0238 and 0.0548, respectively. The rate constant k_1 was computed to determine the fluoride adsorption rate.

$$Slope = -\frac{k_1}{2.303} = -0.0238$$

$$\boldsymbol{k_1 = 0.0548}$$

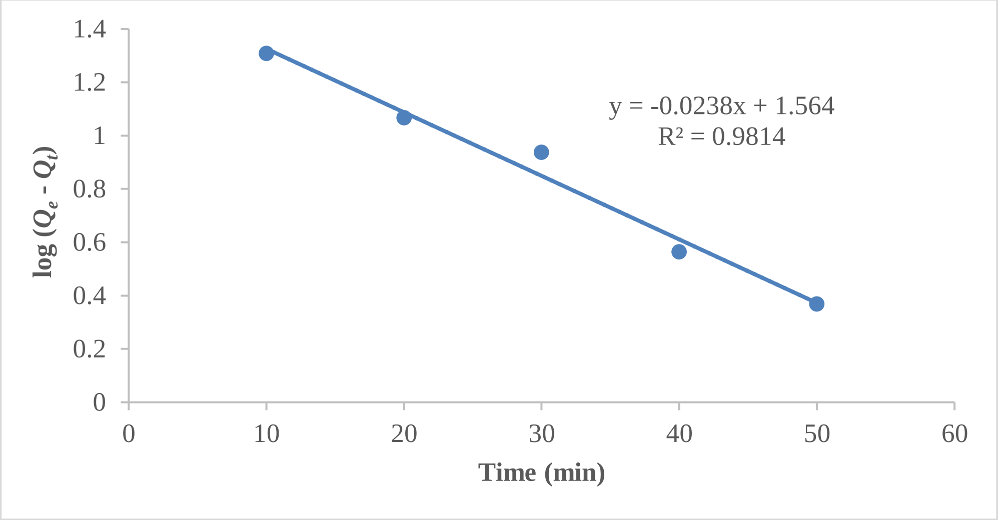


Figure 4.14: Plot of Pseudo-first-order Kinetic Model

4.6.2 Pseudo-second-order Kinetic Model

Equation 4.5 represents the Pseudo-second-order kinetic formula,

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (4.5)$$

Based on Figure 4.15, the graph plotted had a slope and y-intercept of 0.0159 and 0.1221 respectively. The rate constant k_2 was computed using y-intercept value to determine the adsorption rate of fluoride ions.

$$y - intercept = \frac{1}{k_2 {q_e}^2} = 0.1221$$

$$\boldsymbol{k_2 = 0.0025}$$

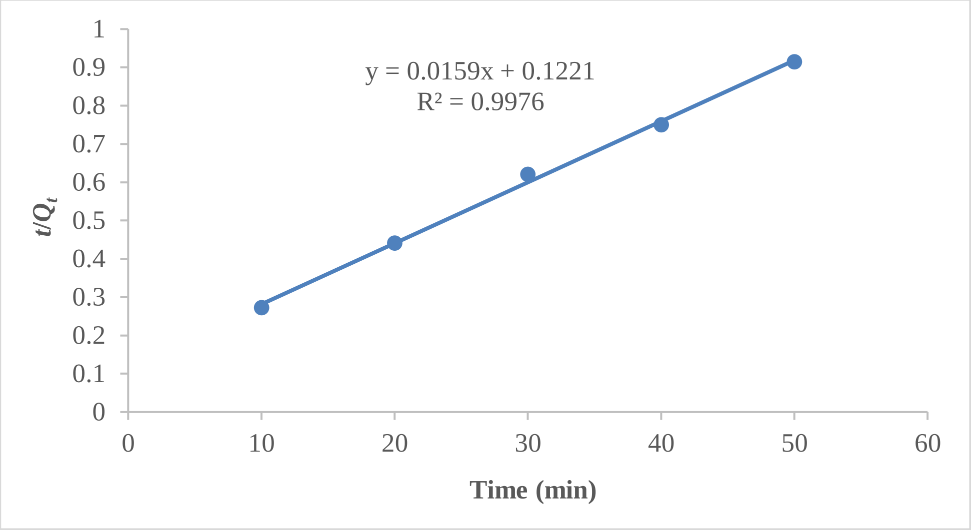


Figure 4.15: Plot of Pseudo-second-order Kinetic Model

In summary, the rate constants k_1 and k_2 computed from the linear plots of first and second order were 0.0548 and 0.0025, respectively. In fact, a larger rate constant k_1 represented faster adsorption rate of fluoride ions. Nevertheless, the larger k_2 rate constant led to the slower the rate of adsorption.

According to Figures 4.14 and 4.15, the correlation coefficients obtained from first and second orders were 0.9814 and 0.9976, respectively, indicating the adsorption of fluoride ions onto SCGA fitted on pseudo-second-order reaction kinetic models. Many researchers have reported the similar results for the fluoride removal. For instance, Chakrapani et al. (2017) determined the adsorption of fluoride onto fruit peel based adsorbent was also best described using pseudo-second-order reaction kinetic model.

4.7 Intraparticle Diffusion

In the adsorption process, the rate of adsorption is often obtained and used to analyse the rate limiting step using intraparticle diffusion model expressed in Equation 4.6:

$$q_t = kt^{1/2} + C \tag{4.6}$$

where,

k = intraparticle diffusion rate constant

Figure 4.16 displays the plot of adsorption capacity Qt against $t^{0.5}$. Although the correlation coefficient showed a relatively straight line plotted ($R^2 = 0.9722$), but the intercept of plotted line failed to pass through the origin (y-intercept = 23.17). This was mainly due the difference in rate of mass transfer in the initial and final stages of fluoride adsorption. In fact, the intercept is an indication of boundary layer thickness. The larger the intercept value is, the greater the boundary-layer effect is. Hence, it could be concluded that intraparticle diffusion was not the only rate limiting step in the fluoride adsorption.

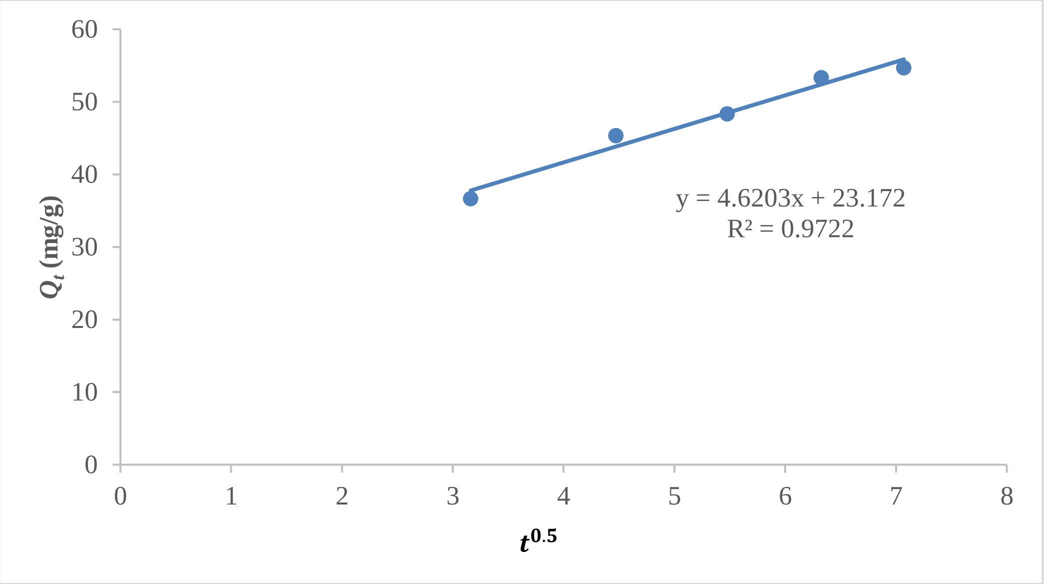


Figure 4.16: Plot of Intraparticle Diffusion

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study has proven that adsorbent prepared using spent coffee grounds is suitable for the removal of fluoride ions in industrial wastewater. The removal efficiencies were significantly influenced by four parameters during the adsorption test. In overall, the highest achievable fluoride removal efficiency 65.6% and adsorption capacity of 188.5 mg F^-/g adsorbent. The results of experiment indicated that the maximum fluoride removal took place at initial concentration of 100 mg/L, 30 mins of contact time, adsorbent dosage of 0.6 g and at slightly acidic or neutral pH (pH = 6) condition.

Besides, surface morphology of SCGA was determined by SEM which presented a developed porous structure with large pore size and high porosity. In addition, the EDX result indicated that the amount of oxygen had greatly reduced, while carbon content was further enhanced after the carbonisation process. The FTIR result showed the elimination of functional groups after carbonisation process and shifting of bands due to the interaction of fluoride ions with the adsorbent functional groups.

Adsorption mechanism of SCGA was best described by Langmuir Isotherm which indicated the monolayer adsorption (chemisorption) of fluoride ions onto the adsorbent. Experimental data plot on adsorption capacity against contact time provided a high correlation coefficient value on the pseudo-second-order kinetic model and hence this model best represented the adsorption kinetics of SCGA.

In fact, there is a huge amount of spent coffee grounds generated globally (6,000,000 tons/year) and pollution hazard arises if discharged to the environment. Hence, by using SCGA as adsorbent for fluoride removal, a total of 4.6×10^5 tons of fluoride ions can be removed. Besides, it can treat a total of $9.3 \times 10^8\ \mathrm{m}^3$ of industrial fluoride wastewater with 500 mg/L of initial fluoride concentration.

5.2 Recommendations for Future Work

As the fluoride adsorption at high fluoride concentration is not preferred, pre-treatment of industrial wastewater with initial fluoride concentration higher than 100 mg/L is needed. Hence, the pre-treatment prior to the adsorption using spent coffee grounds requires further research. Besides, further studies can be carried out using SCGA to remove heavy metals and dyes in industrial wastewater which also greatly contribute to the environmental pollution.

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APPENDICES

Appendix A: Tables

Table A1: Experimental Data for Study of Initial Concentration Against Contact Time

Contact Time (min)	Removal Efficiency (%)			Adsorption Capacity (mg/g)		
Initial Concentration (mg/L)	**100**	**300**	**500**	**100**	**300**	**500**
10	55	47	41.4	18.33	47	69
20	59.4	55	51.8	19.8	55	86.33
30	62	58	56	20.67	58	93.33
40	63.5	58.7	56.6	21.17	58.67	94
50	62	60	57	21	59.8	95.1

Table A2: Experimental Data for Parameter Study on Adsorbent Dosage

Adsorbent Dosage (g)	**Removal Efficiency (%)**	**Adsorption Capacity (mg/g)**
0.15	56.54	188.47
0.3	58	96.67
0.45	60.32	67.02
0.6	51.4	51.40
0.75	41.6	41.60

Table A3: Experimental Data for Parameter Study on pH of wastewater

pH	**Removal Efficiency (%)**	**Adsorption Capacity (mg/g)**
2	60.34	100.57
4	62.20	103.67
6	61.76	102.93
8	58.80	98
10	54.20	90.33

Table A-4: Langmuir Isotherm Result

Initial Fluoride Concentration (mg/L)	**Equilibrium Concentration, *Ce* (mg/L)**	**Adsorption Capacity, *Qe* (mg/g)**	***Ce* / *Qe***	**Separation Factor, R_L**
100	37	10.5	3.52	0.83
200	78	20.3	3.84	0.72
300	124	29.3	4.23	0.63
400	171	38.2	4.48	0.56
500	220	46.7	4.71	0.5

Table A-5: Freundlich Isotherm Result

Initial Fluoride Concentration (mg/L)	**Equilibrium Concentration, Ce (mg/L)**	**log Qe**	**log Ce**
100	37	1.02	1.57
200	78	1.31	1.89
300	124	1.47	2.09
400	171	1.58	2.23
500	220	1.67	2.34

Table A-6: Pseudo Kinetic Model Experimental Data

Time (min)	$Q_e - Q_t$	**log** $(Q_e - Q_t)$	t / Q_t
10	20.33	1.31	0.27
20	11.67	1.07	0.44
30	8.67	0.94	0.62
40	3.67	0.56	0.75
50	2.33	0.37	0.91

Appendix B - Figures

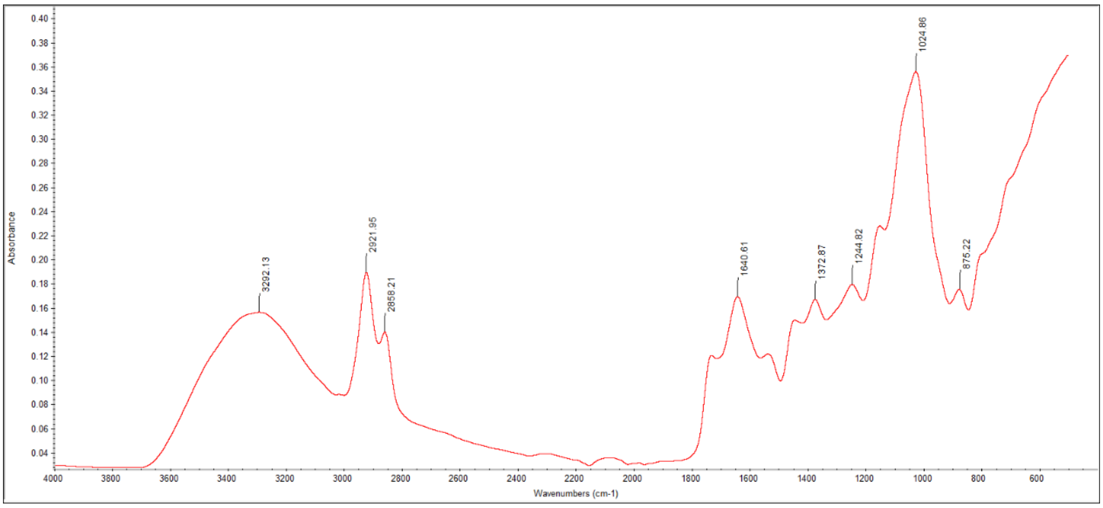

Figure B-1: FTIR Spectra of Raw Spent Coffee Ground (SCG)

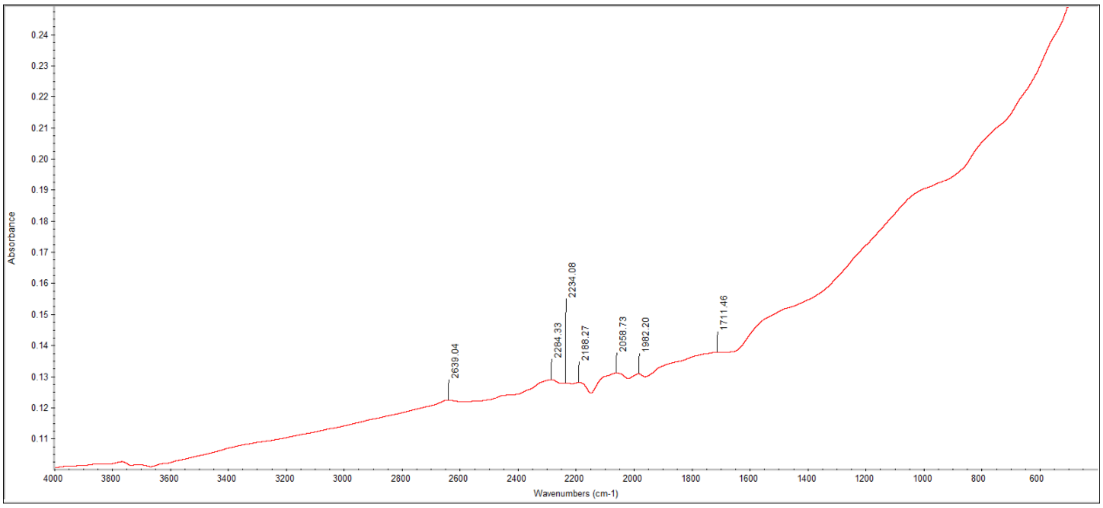

Figure B-2: FTIR Spectra of SCGA Before Fluoride Adsorption

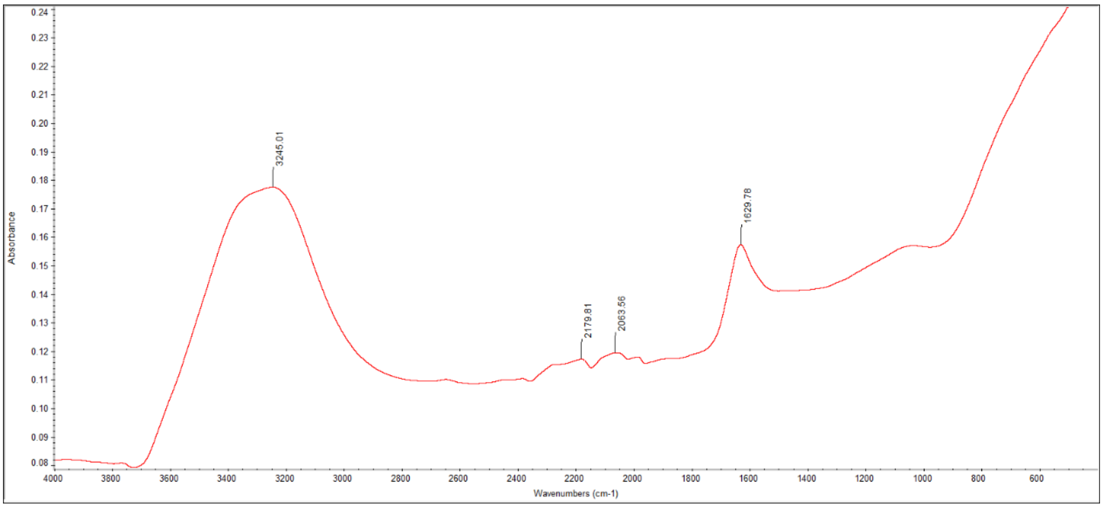

Figure B-3: FTIR Spectra of SCGA After Fluoride Adsorption

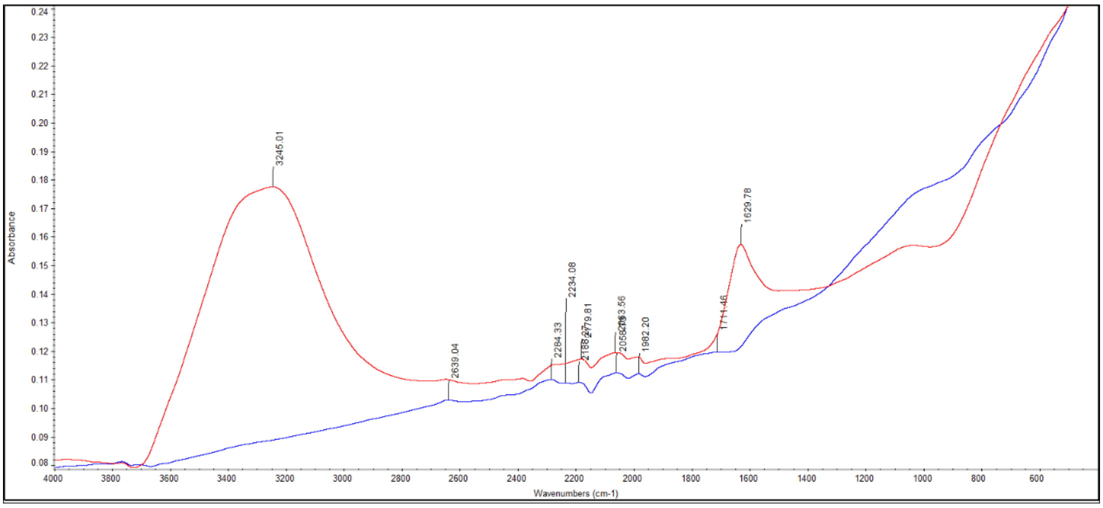

Figure B-4: Comparison on FTIR Spectra of SCGA Before and After Fluoride Adsorption

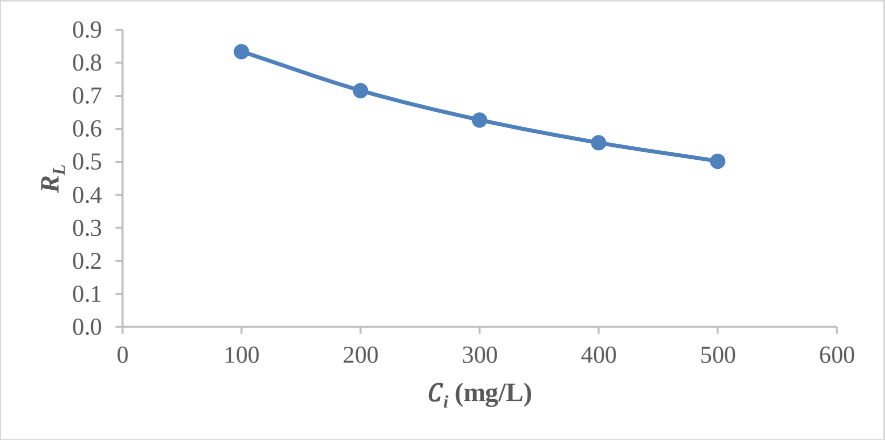

Figure B-5: Plot of Separation Factor R_L against Initial Fluoride Concentration