

**JIMMA UNIVERSITY**  
**COLLEGE OF NATURAL SCIENCES**  
**DEPARTMENT OF CHEMISTRY**



**A THESIS ON**  
**REMOVAL OF FLUORIDE USING POLYANILINE MODIFIED PUMICE**  
**FROM AQUEOUS SOLUTIONS**

**BY**  
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***OCTOBER, 2019***  
***JIMMA, ETHIOPIA***

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FROM AQUEOUS SOLUTIONS**

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**A THESIS SUBMITTED TO JIMMA UNIVERSITY DEPARTMENT OF  
CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY**

**OCTOBER, 2019**

**JIMMA, ETHIOPIA**

## **Declaration**

I, Hereby, declare that this thesis is my original work, that it is the documentation of work carried out by me and that it has not been submitted in any previous application for a higher degree. I announce that I have developed and written the enclosed master thesis completely by myself, and have not used sources or means without declaration in the next. Any thoughts from others or literal quotations are clearly marked. The master thesis was not used in the same or in similar version to achieve an academic grading or is being published elsewhere. This has been submitted in partial fulfillment of the requirement for M.Sc. degree at Jimma University. I declare that this thesis is not submitted to any other institution anywhere for the award of academic degree. Wherever contribution of others are involved, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement source made.

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## **Acknowledgement**

In the beginning, I would like to give my great thanks to God, the almighty for his showers grace and blessing throughout my research. I would like to express my sincere gratitude to my advisor Dr. Fekadu Melak for his continues guidance, care, moral support and encouragement throughout my research work. My deepest gratitude also goes to my co-advisor Mr. Abebe Diro for his helpful discussion, suggestion and encouragement throughout this work. I am also thankful to Mr. Menberu Yitbarek for his assistance in using Fluoride Ion Selective Electrode for my samples. I gratefully acknowledge also Department of Chemistry, Jimma University for its unreserved help and encouraging me by providing necessary materials.

Finally, I would not forget to give abundant thanks to anyone that supports me morally, financially and technically throughout the research of my master degree.

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## List of Abbreviations

EPA	Environmental Protection Agency
FISE	Fluoride Ion Selective Electrode
HDPE	High-Density Polyethylene
LDCs	Less Developed Countries
MCL	Maximum Contaminant Levels
NEERI	National Environmental Engineering Research Institute
WHO	World Health Organization

## **Abstract**

Fluoride is among the most common ground water contaminants that can cause human health impact when it is found above the permissible limit. Therefore, in this study, polyaniline modified natural pumice was used for fluoride removal. Adsorption influencing parameters including pH, contact time, dose of adsorbents were optimized. The residual fluoride after adsorption was analyzed through back titration method. Results of the study revealed that 14 mg/g maximum adsorption capacity was obtained using polyaniline modified pumice at optimal conditions of solution pH 2.0, contact time 1h, adsorbent dose of 4 g/L. It was found that fluoride sorption kinetic was fitted to pseudo-second-order model. Polyaniline modified pumice was found to be an alternative adsorbent for the removal of fluoride from water.

**Keywords:** Pumice, Polyaniline, Adsorption capacity, fluoride removal

# Chapter 1

## 1. Introduction

Fluorine is not found as a free element in nature due to its reactivity with other minerals, and the most common are fluorspar, cryolite, fluorapatite, and sellaite ( $\text{MgF}_2$ ) [1]. It is one of the essential anions in water and food. Naturally, fluoride comes from water when other minerals such as fluorite  $\text{CaF}_2$ , cryolite  $\text{Na}_3\text{AlF}_6$  and fluorapatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  dissolved in water.

Fluoride is naturally found at varying concentrations from trace to high level in all drinking water [2]. It has been shown to cause significant effects in humans through drinking water [3]. Fluoride has beneficial effects on teeth at low concentrations in drinking water (0.5–1.0 mg/L), especially for young children in that it promotes calcification of dental enamel and protects teeth against tooth decay [4]. When fluoride level is small (1–1.5 mg/L) in drinking water, formation of fluoroapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) which is resistant to acid attack leads to prevention of dental caries [5]. The mechanisms of fluoride in dental caries prevention are; reducing the enamel solubility caused by acid, lowering the enamel surface permeability and inhibiting the fermentation of carbohydrates by microorganisms of the oral cavity [5].

Excessive levels of fluoride ( $>1.5$  mg/L) can cause several problems ranging from mild dental fluorosis to crippling skeletal fluorosis and non-skeletal fluorosis including neurological, allergic, gastro-intestinal, bone cancer and urinary tract conditions, impaired kidney function, digestive and nervous disorders, reduced immunity, Alzheimer's disease, and adverse pregnancy outcomes [6]. Skeletal fluorosis was first reported in Ethiopia in 1973 in the Wonji Shoa sugar estates in the Ethiopian Rift Valley [7]. Initial results from a programme to measure fluoride in wells from all over Ethiopia found that, from the 138 wells tested, 33 percent had fluoride concentration greater than 1.5 mg/L; the maximum level detected was over 11.5 mg/L [8].

The maximum permissible level for fluoride in potable drinking water is 1.5 mg/L, according to the World Health Organization [9]. The water interaction and volcanic rock activity were considered as the most effective factors for increasing the fluoride concentration in water. In Ethiopia, well water, spring water, and Tap water are the common water supply source used in

both urban and rural areas [10]. The concentration of fluoride in drinking water resembles a two-edged knife. That is both trace and high concentrations of it are harmful [11, 12].

Various techniques have been proposed for fluoride removal from water including adsorption, membrane separation, ion-exchange, precipitation/coagulation, nanofiltration and electrolytic defluoridation [13, 14]. Precipitation and coagulation are expensive and produce high amounts of sludge or secondary pollutants which need additional treatments. Membrane processes are limited by fouling problems, and thermal processes are costly [5]. Ion-exchange is more expensive removal technique and ion interfering is another difficulty facing it, and formation of toxic solid waste involved during the process. Among these methods, adsorption is considered as economical and can remove ions over a wide range of pH to a lower residual concentration. It is an appropriate technique compared to others, for small community water source defluoridation. Additionally, adsorption is a common process that has been used extensively, because of its simplicity of design and operation, effectiveness, insensitivity to toxic substances and the availability of a wide range of adsorbents.

Since the investigation of fluoride adsorption using polyaniline modified pumice has not yet been reported. Polyaniline has reactive N-H group which is the basis of amine and imines multi functionalities. This poly functionality made it suitable for adsorption applications. Moreover, polyaniline is distinguished by easy synthesis and high environmental stability [15].

The focus of this research is to prepare conducting polymer by surface coating of pumice with polyaniline by chemical process and investigating its adsorption capacities for removal of fluoride due to the fact that the pumice is a very abundant and inexpensive material.

## **1.2. Statement of the problem**

Occurrence of fluoride above the WHO recommended level in drinking water is a global concern in reducing health risks introduced by its consumption. Several fluoride removal techniques are available including adsorption, precipitation, coagulation, ion exchange, filtration, membrane separation, electrodialysis and reverse osmosis [5, 11, 13]. Due to the major downsides of most methods, adsorption has been employed in this study. Adsorption techniques have been shown promising, however, looking for low-cost and available adsorbents with high removal capacity is yet vital. If adsorbents are wisely selected adsorption could be the preferred option in developing countries to remove fluoride from water. Since, polyaniline has no report of toxicity and possess amine group which can easily converted to positive surface in acidic medium, it was suggested as modifier in this thesis for removal of fluoride, a negatively existing species in water.

### **1.3. Objectives**

#### **1.3.1. General objective**

To evaluate adsorptive capacity of polyaniline modified pumice for the removal of fluoride from aqueous solutions.

#### **1.3.2. Specific objectives**

- To prepare polyaniline modified pumice, as adsorbent
- To optimize adsorption influencing parameters including: pH, contact time, adsorbent dosage and concentration variation
- To investigate the adsorption capacity of the adsorbent for fluoride removal
- To compare the observed results with some of the previously reported data.

### **1.4. The significance of the study**

The method will pave a way for other researchers in acquiring information on modifying pumice surface by polyaniline for removal of fluoride from aqueous solutions at room temperature where the optimal time, pH, and adsorbent dose had been figure out.

## Chapter 2

### 2. Literature Review

#### 2.1. Natural existence of fluoride ion

Volcanic rocks and Precambrian rocks are the most suppliers of fluoride in nature [16].

Fluoride form about 0.08% of the earth's crust, and it existed in form of minerals, geochemical deposits and it enters the food chains via drinking water, consumption and cereals. Fluoride concentration snake into water physically while degradation of fluoride presence in the rocks [17]. On the whole, because more contact time of groundwater with stone bed, the concentration of fluoride in groundwater is more than surface water [18]

#### 2.2. Artificial source of fluoride

Fluoride formed compounds with iron, aluminum, and beryllium as fluoride ion in natural waters; the waste which comes out of bricks, tiles, and ceramics contains fluoride and it enters water bodies that we received. Some of the inorganic materials used in the industries possess fluoride ions such as a flux in the steel and glass fiber, fluorosilicic acid  $H_2SiF_6$ , sodium hexa fluorosilicate  $Na_2SiF_6$ , and sodium fluoride are used in public water fluoridation treatment [19].

#### 2.3. Toxicity of fluoride

Fluoride toxicity exists either naturally or anthropogenic [20]. Naturally the groundwater reported a high concentration of fluoride; especially when it used for household consumptions; since most of the area depends on direct intake of the groundwater which possesses high content of fluoride, their expose to such amount of fluoride for a period may be led to health problem [21]. In addition, anthropogenic sources such as infiltration of chemical fertilizers in agricultural areas and liquid wastes from industrial entities also contribute to fluoride ions in groundwater [22]. Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity which results in dental, skeletal and no skeletal forms of fluorosis i.e. high fluoride ingestion, in children as well as adults. Constant and frequent contact with fluoride results in a condition in the body called enamel fluorosis. We can see the impact of fluoride in a



mild colorization of dental surfaces to sever staining, enamel loss, and pitting. These conditions remain permanent in the body after dentification in childhood from birth till 8 years of age.

Fluorosis in mild version can be evidenced by mottling of teeth and in high version by embrittlement of bones and neurological damage [23]. Dental fluorosis is a life-long handicap. Skeletal fluorosis is the accumulation of fluoride in skeletal tissues associated with pathological bone formation. Symptoms include joint pains, progressive stiffness and limitation of mobility leading to severe invalidity (crippling skeletal fluorosis) [22]. In areas where children have poor nutrition, or lack calcium, high fluoride can lead to deformity of the lower limbs. Workers exposed to high fluoride concentration areas are diagnosed with bladder cancer [23]. However, fluoride can be considered as an essential mineral in the range of low consumption. Some reports are indicated below in Table 1.

**Table 1.** Showing influence of fluoride concentration on human health [1, 3].

Fluoride concentration in mg/L	Health effects
< 0.5	Dental Carries
0.5 – 1.5	Optimum dental health
1.5 – 4	Dental fluorosis
4.0 – 10	Dental and skeletal fluorosis
> 10	Crippling fluorosis

## 2.4. Fluoride Removal Techniques

Coagulation and precipitation with 3-valent iron and aluminum, ion exchange, reverse osmosis, membrane process, adsorption, and electrochemical techniques are among the methods of removing fluoride from drinking water [24].

### 2.4.1. Precipitation/coagulation

In this method, fluoride removal from water is mediated by calcite,  $Mg(OH)_2$ ,  $Al(OH)_3$ ,  $Fe(OH)_3$  floc formation. The principle involved in this technology is that the fluoride ions adsorb on the flocs and are then subsequently removed either simultaneous or in succeeding treatment

units such as sedimentation, fixed bed or microfiltration unit. The aim of coagulation is to coagulate suspended materials and especially semi-dissolved and colloid forms into large pieces using chemicals which precipitate by their weight. In other words, coagulation accelerates precipitation phase in mechanical treatment. The method involves the addition of alum and lime into water followed by rapid mixing. After some time, the stirring intensity is reduced and this induces floc formation that is subsequently removed by simple settling.

For example, in a co-precipitation technique, the so called ‘Nalgonda technique’, calculated quantities of alum, lime and bleaching powder are mixed with water, after mixing the water is processed with flocculation, sedimentation, filtration and disinfection. The entire operation takes about 2–3 hours for around 200 people in batches. Nalgonda technique is widely used in India because of its simplicity and cost effectiveness. However, the production of excess sludge is a concern [14]. Disadvantages of this technique are reported that treated water has high residual aluminum concentration (2–7 mg/L) than the WHO standard of 0.2 mg/L.

According to the report of the National Environmental Engineering Research Institute (NEERI) of Nagpur, India, the technique is applicable to different levels of water treatment. On a small scale (household), the chemicals are introduced in buckets or drums, while on a medium scale for a small community, a fill-and-draw plant is used. For large-scale operation, a process combining mixing, flocculation and sedimentation is used. Although precipitation is an economical and a robust technique in the removal of fluoride from water, the technique has been found to suffer from excessive sludge generation and dewatering such sludge has proven to be difficult. Since the solid size and content are extremely small and low, respectively; instability of the sludge under adverse environmental conditions has too been reported and in most cases, achieving the maximum contaminant level has been found to be difficult (Table 2).

Therefore, the technique is only suited to centralized water treatment system and has not been very attractive to many end users [12].

#### **2.4.2. Membrane techniques**

Membranes are thin materials that moderate the transport of species through them depending on their physical or chemical properties. These components are critical elements in water purification, including desalination, decontamination, and disinfection. The aim for membranes

in is to remove undesirable species, including ions, solutes, pathogens, and particles, while allowing water to pass through.

Basic advantages arising from the application of membrane processes are: production of water of invariable quality, smaller quantity of added chemical substances, lower consumption of energy, compactness of the installation, possibility to effect full automation of the process. However, Fouling arising from feed water characteristics is a major problem and due to high quantity of water rejection typically between 35% and 65%, it is not suitable to regions where water is scarce (Table 2). Moreover, brine discharge from RO plant is highly concentrated and requires treatment. The technique also involves a high investment cost, requires high technology for operation and maintenance and therefore does not suit developing countries [12].

#### **2.4.3. Ion - exchange (IE) technique**

Ion-exchange resins are most commonly used in water treatment processes to soften the water supply by exchanging sodium ions for “hardness” ions including calcium and magnesium. Ion-exchange filters exchange the major ions present in the water, removing fluoride and other ions in water. Selective fluoride removal can be performed using the calcium form of strong acid cation exchange resin. The calcium forms an insoluble complex with the fluoride in water with low to high salt concentrations. Soluble anions such as sulfate, arsenic, selenium and nitrate and TDS can compete with fluoride and can affect the run length. Some of the limitations to the use of ion exchange include the production of a highly concentrated waste by-product stream that poses a disposal problem (this problem can be reduced by brine recycling) [24]. Run length is affected by sulfate level. The technology is only recommended primarily for small groundwater systems with low sulfate and low TDS. Another limitation to its use is that it requires a high level of operator skill and therefore not popular with many end-users (Table 2).

#### 2.4.4. Adsorption technique

The principle behind this technique is that a component (fluoride in our case) is transported by diffusion from the bulk phase to the solid surface where it is bound at the surface or interface between two phases by either chemical or physical forces.

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid or liquid–solid interface. Adsorption process is a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds. On the other hand, adsorption process involves two components; adsorbent and adsorbate. Adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent.

Adsorption is one of the most widely used techniques for removing water-soluble ions such as fluoride. Around 100 different types of adsorbent have so far been used to absorb fluoride, such as alumina and alumina-based adsorbents, adsorbents based on iron and calcium, oxides and metal hydroxides, impregnated metal oxides, carbon-based adsorbents, natural materials used as adsorbents, bioadsorbents, agricultural and industrial waste, apatite and hydroxyapatite, building materials, and nanoadsorbents [11].

In recent years, the use of inexpensive natural adsorbents in natural or modified form in the removal of water contaminants has received attention. Natural pumice (NP), and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  modified pumice (FEMP), and hexadecyltrimethyl ammonium bromide (HDTM.Br) modified pumice (HMP) have been used for fluoride removal in maximum removal efficiency of 9.39, 76.45, and 95.09% for NP, FEMP, and HMP, respectively [25]. The findings of another study showed that the use of pumice stone modified with  $\text{MgCl}_2$ , and a maximum efficiency of fluoride removal of 68.4% from an aqueous solution was obtained at the optimal pH of 6 [26]. Using pumice stone modified with HDTMA, and the concentration of 10 mg/L of fluoride was removed at the optimum pH of 6 with an efficiency of 96%.

Using an inorganic phosphate mineral called brushite, the removal efficiency was also obtained 88.78% at a pH of 5.36 with the maximum adsorption capacity of 29.21 mg/g. In one

other research, fluoride was removed using hydroxyapatite at a pH of 4.16 with a removal efficiency of 86.34% and with the maximum adsorption capacity of 3.12 mg/g [27].

**Table 2.** Summary of fluoride removal technology screening [22].

Screening strategy	Coagulation and precipitation	Membrane processes	Ion-exchange	Adsorption
▪ Cost	Low	High	Medium	Low
▪ Regulatory compliance	MCL achievable	not MCL achievable	MCL achievable	MCL achievable
▪ Appropriateness	Nalgonda method applicable to LDCs	Not appropriate to LDCs	Not appropriate to LDCs	Appropriate to LDCs and is versatile
▪ Environmental burden	Difficult to dewater sludge	Water rejection high	Highly concentrated brine	Non hazardous waste

## 2.5. Polyaniline

Polymer is a large molecule composed of repeating structural units connected by covalent chemical bonds and widely applied for water purification. It gives lower coagulant, less volume of sludge and it raises uptake of ions from water. For example, polyaniline is an oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. Polyaniline can be chemically synthesized by the oxidative polymerization of aniline monomer in the presence of aqueous acid, e.g., 0.1M HCl solution [28, 29]. There are many different oxidizing agents for the production of polyaniline from aniline, including: ammonium peroxydisulfate, hydrogen peroxide, and ferric chloride [30].

### 2.5.1. Application of polyaniline

Polyaniline is an intrinsic conductivity and a remarkable ability to undergo reversible changes from conducting form to semiconducting form and to a dielectric form. Polyaniline is easy to synthesize and shows a high stability in the environment. One of the applications of polyaniline was in the structure of light batteries which have been developed with respectable performance using polyaniline as positive electrode (cathode) and lithium-aluminum alloys as negative electrode (anode). Polyaniline also has been used in the field of biomedical applications; on this line, biosensors have been developed starting with immobilization of the enzymes on a conducting polyaniline matrix [31]. The color change property associated with polyaniline in various oxidation/reduction states has found potential uses in electrochromic devices, smart window [32].

## 2. 6. Adsorption kinetics studies

Adsorption is a time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing fluoride in water. In many cases, the kinetics of adsorption based on the overall adsorption rate by the adsorbents is described by the pseudo first-order and pseudo second-order.

The pseudo first-order rate expression [33] is given as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \dots\dots\dots (1)$$

Where  $q_e$  and  $q_t$  are the amount of fluoride adsorbed on adsorbent at equilibrium and time,  $t$ , respectively, (mg/g).  $k_1$  is the rate constant of first order adsorption ( $\text{min}^{-1}$ ).

Integrating equation (1) for the boundary conditions  $t = 0$  to  $t = t$  is the following:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots (2)$$

The plot of  $\log (q_e - q_t)$  versus  $t$  will give a straight line and the value of  $k_1$  can be obtained from the slope of the graph.

The second-order kinetic model is expressed as:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \dots\dots\dots (3)$$

Where,  $k_2$  is the pseudo-second-order rate constant of adsorption (g/ mg min). The linearised integrated form of (3) is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \dots\dots\dots (4)$$

If the pseudo second-order kinetics is applicable to the system, then the plot of  $\frac{t}{q_t}$  versus  $t$  of equation 4 will give a linear relationship with  $\frac{1}{q_e}$  and  $\frac{1}{k_2 q_e^2}$  as a slope and intercept respectively.

The values of  $q_e$  and  $k_2$  can be determined from the slope and intercept and there is no need to know any parameters beforehand. The pseudo second-order kinetics model has been successfully applied to several biosorption systems as reported by [11].

## Chapter 3

### 3. Materials and Methods

#### 3.1. Chemicals and materials

NaF (Finkem, Italy), aniline ( $C_6H_7N$ ),  $FeCl_3 \cdot 6H_2O$  (Supertekchemicals, England),  $C_3H_6O$  (Supertekchemicals, England), NaOH (Labmerk chemicals, India), HCl (Riedel-De Haen, Germany), glacial acetic acid ( $CH_3COOH$ , Riedel-de Haën, Germany), ammonia (Philip Harris, England), ammonium chloride (Philip Harris, England), disodium EDTA salt (Chemika, Mumbai), NaCl (Fischer scientific, Germany) and  $CaCl_2 \cdot 2H_2O$  (Supertekchemicals, England) chemicals were used throughout the experiment.

Total Ion Strength Adjustment Buffer (TISAB) was prepared to use ISE. Distilled water was used for preparation of all solution and dilution series. Whatman filter paper (grade 1 and size 8.5 cm); from Whatman International Ltd, polyethylene plastic bottles, plastic syringe, funnel, sampling container, stirrers and classical glass wares, sieve, volumetric flasks, digital analytical balance and pH meter were used as equipments.

#### 3.2. Solution preparation

The analytical grade reagents were used in this study. A stock solution of 1000 mg/L fluoride was prepared by dissolving 2.21 g of NaF in distilled water and stored with polyethylene plastic bottles. Calibration standards were prepared from 1000 mg/L fluoride stock solution. 100 mg/L calcium was prepared by dissolving 3.68 g of  $CaCl_2 \cdot 2H_2O$  in distilled water. 0.005 M of disodium EDTA salt was prepared by dissolving 1.86 g of disodium EDTA salt in 1L distilled water. Working solutions of fluoride were prepared by diluting the stock solution prior to each experiment. The applicability of the adsorbent was investigated for various parameters. EDTA was used as a suitable titrant for the excess calcium added. Moreover, to convince the method, fluorides remain as residue was determined using fluoride ion selective electrode. Total ionic adjustment buffer (TISAB) was prepared by mixing 4 g disodium EDTA salt, 58 g NaCl, and 57 mL of glacial acetic acid in a 1 L volumetric flask and stirring to dissolve the compounds [6,41]. Then, 125 mL of 6 M NaOH was added to adjust the pH to a value between 5 and 5.5,



and the flask was filled to the mark with double-distilled water. The amount of fluoride removal in case of concentration variation was determined using the fluoride ion selective electrode in a 1:1 mixture of sample and buffer (TISAB). Therefore, 20 mL of the sample and 20 mL of TISAB solution were mixed and then stirred for 3 min with a magnetic stirrer. Then, the electrode potentials of sample solutions were compared with those of fluoride standards and the amount of fluoride in sample was determined.

### **3.3. Preparation of unmodified pumice**

Pumice used in the study was obtained from Rift valley area of Eastern Shoa, Ethiopia. To enhance the porosity of Pumice and also to remove its impurities, Pumice was washed several times with distilled water, followed by acetone, and then dried in air at room temperature for 12 hours. Finally, the raw sample was grounded by a primary crusher (hammer type), and then sieved to particle size fraction of 300 mesh screen [11].

#### **3.3.1. Surface coating of pumice with polyaniline**

10 g of pumice was taken and soaked in a 0.2 M HCl solution. 150 mL of a 0.5 M aqueous aniline solution was added to the flask containing acidified pumice on stirring for 30 min to homogenize the system; after that, 150 mL of equimolar  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution was added to drop wise to initiate oxidative polymerization on a continuous stirring. To terminate polymerization process it was putted at room temperature until 12 hours. After the reaction terminated, the formed greenish black polyaniline coated pumice was filtered, and then washed with excess dilute HCl solution thoroughly followed by distilled water until the filtrate became colorless to remove impurities. Finally it was dried by oven at  $60^\circ\text{C}$  for 48 hours.

#### **3.3.2. Characterization of adsorbents**

Fourier transform infrared (FT-IR) spectra of dried unmodified and modified adsorbents were recorded at  $400\text{-}4000\text{ cm}^{-1}$  wave number range using a Spectrum 65, Perkin Elmer model FT-IR spectrophotometer to determine the surface functional groups.

### 3.4. Adsorption study

Fluoride adsorption experiments were conducted in order to determine the efficiency of adsorbent and the effect of controlling parameters like contact time, pH, dose and initial concentration. A batch adsorption experiments were carried out in 50 cm<sup>3</sup> high-density polyethylene (HDPE) bottles. The adsorption study was carried out by contacting 0.25 g of the polyaniline modified pumice with 25 mL of 100 mg/L fluoride solution under different conditions. All experiments were carried out triplicate, and the concentrations given are average values. The sorbent was added to the solution in the bottles, and proper shaking was achieved for the mixture at room temperature for 60 minutes. The aqueous phase was separated from the sorbent through filtration. The residual fluoride was analyzed through back titration method to know the effect of pH, contact time and dosage. However, concentration variation was analyzed by FISE to convince the method. The amount of adsorption at t,  $q_t$  (mg/g), was calculated using the following relation [34]:

$$q_t = \frac{(C_o - C_t)}{m} V \dots\dots\dots (5)$$

Where,  $C_o$  is initial concentration of fluoride in the solution (mg/L),  $C_t$  is concentration of fluoride at time t (mg/L), V is the volume of solution (L), and m is the mass of dry adsorbent (g).

The amount of equilibrium adsorption,  $q_e$  (mg /g), was calculated using the formula [35].

$$q_e = \frac{(C_o - C_e)}{m} V \dots\dots\dots (6)$$

Where,  $C_o$  and  $C_e$  are the initial and equilibrium concentration of fluoride in the solution (mg/L), respectively.

The removal percentage adsorption of fluoride was calculated using the following equation [36]

$$\% \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \dots\dots\dots (7)$$

### **3.5. Effect of Parameters**

#### **3.5.1. Effect of contact time on adsorption**

The adsorption of fluoride from water by polyaniline modified pumice was studied at various time intervals (10-120 min) and at a concentration of 100 mg/L fluoride solution. This was done by weighing 0.25g of polyaniline modified pumice into each 50cm<sup>3</sup> HDPE bottles and 25 mL of 100 mg/L of fluoride solution was introduced into it. The mixture was shaken by a mechanical shaker at room temperature for varying periods of time. The solutions in the HDPE bottles were filtered by Whatman filter paper at different time intervals from the first to the last bottle. The filtrates were then taken for analysis using back titration with EDTA by adding excess calcium. During titration, 10 mL of equimolar calcium and fluoride solutions (100 mg/L) were mixed together and settled to 12 hours to form precipitation. Then, to reduced CaF<sub>2</sub> precipitation, again filtered and titrate with 0.005M EDTA. The titration was done by adding buffer solution. Finally, the amount of fluoride adsorbed was calculated for each sample to get optimum contact time.

#### **3.5.2. Effect of pH on adsorption**

The effect of pH on the adsorption of fluoride was carried out within the range (pH 2-10.8). This was done by contacting 0.25g of polyaniline modified pumice with 25 mL of 100 mg/L fluoride solutions in a 50cm<sup>3</sup> HDPE bottles. The pH of each solution was adjusted by the desire value by dropwise addition of 0.1M HCl and/or 0.1M NaOH. The solutions were filtered by Whatman filter paper. The filtrates were then taken for analysis using back titration with EDTA by adding excess calcium. Finally, the optimum pH was determined as the pH with the highest adsorption of each fluoride solutions.

#### **3.5.3. Effect of adsorbent dosage**

The adsorption of fluoride at different adsorbent doses (0.1–0.4g) was investigated. This was done by weighing 0.1, 0.15, 0.2, 0.25, 0.3, 0.35 and 0.4g of modified pumice into each HDPE bottles and 25 mL of 100 mg/L of fluoride solutions at optimal pH and contact time.

The solutions in the HDPE bottles were filtered by Whatman filter paper. The filtrates were then taken for analysis using back titration with EDTA by adding excess calcium.

Finally, the optimum dosage was determined as the dose with the highest adsorption of each fluoride solutions.

#### **3.5.4. Effect of initial concentration on adsorption**

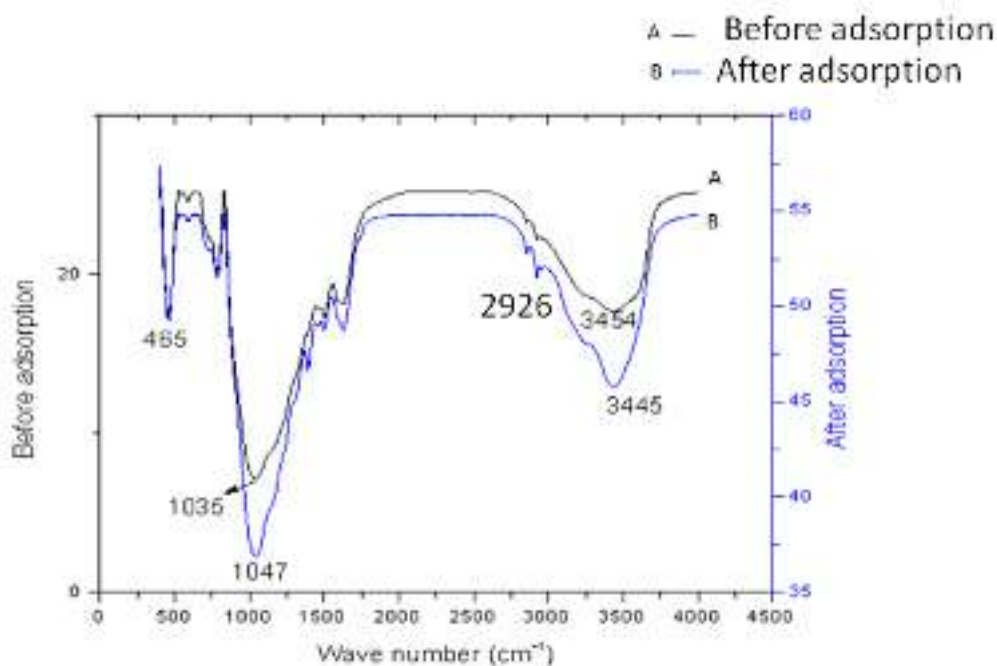
Batch adsorption study of fluoride was carried out using concentration range of 1.5 to 100 mg/L. This was done by introducing optimum conditions of contact time, pH and dose, respectively of modified pumice into each of the HDPE bottles. Then, to convince the method, the concentration of residual fluoride ion in each solution was determined using FISE. Finally, the optimum concentration was determined as the concentration with the highest adsorption of fluoride solutions.

## Chapter 4

### 4. Result and discussion

#### 4.1. Characterization of the adsorbent

FT-IR spectroscopy is a useful tool to identify functional groups in a molecule as each specific chemical bond often has a unique vibration energy absorption band and can obtain structure, bond information, study of strength and fraction of hydrogen bonding.

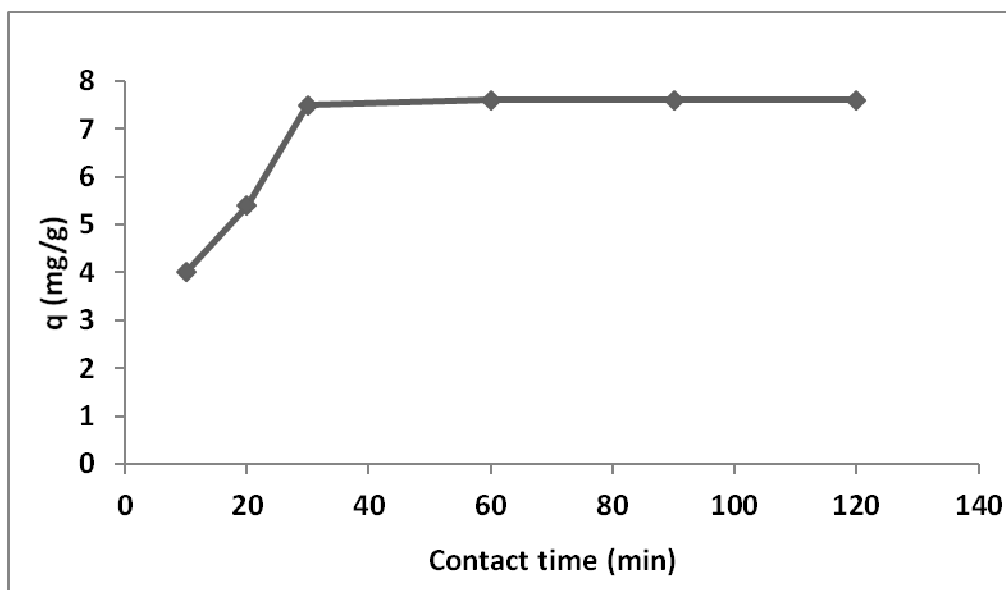


**Figure 1.** FT-IR data of the adsorbent before and after adsorption

Figure 2 represents FTIR spectra for adsorbents. The presence of broad peaks at 3454 and 3445 cm<sup>-1</sup> are associated with the N-H stretching vibrations, before and after adsorption, showing intensity and frequency shifts upon adsorption of fluoride. The presence of weak absorption band at 2926 cm<sup>-1</sup> corresponding to C-H stretching of the CH<sub>2</sub> group. The peak at 1035 cm<sup>-1</sup> and 1047 cm<sup>-1</sup> indicates the presence of C-O stretching vibrations.

## 4.2. Effect of contact time on adsorption

The effect of contact time was checked by keeping the other factors such as pH, adsorbent dosage and initial fluoride concentration at the constant value. The variations of fluoride adsorption were conducted by varying contact time (10–120 min) with a dose of 10 g/L and initial fluoride concentration 100 mg/L at room temperature (Figure 2).

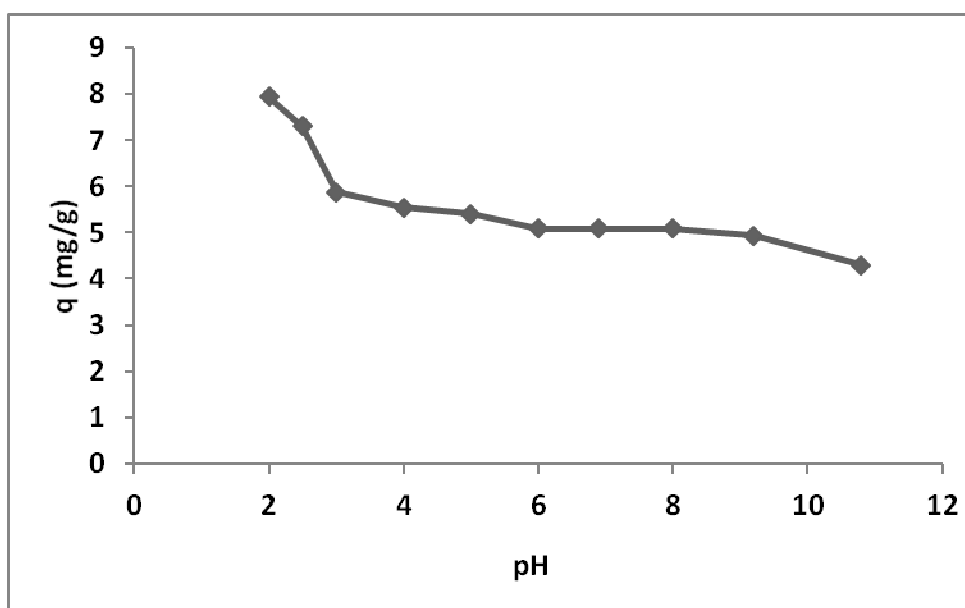


**Figure 2.** Effect of contact time for adsorption of fluoride using modified pumice; (initial concentration 100 mg/L and adsorbent dose 0.25g at room temperature)

Figure 2 shows that the removal capacity of fluoride from water using polyaniline modified pumice was very rapid during the first 60 min, and thereafter, the rate of fluoride adsorption remained constant. Initially, there were large number of vacant active binding site in the adsorbent and consequently large amounts of fluoride were bound rapidly onto the adsorbent. There was no further significant increase in the uptake capacity of fluoride after 60 min. The binding site shortly became limited and the remaining vacant surface sites could not be occupied due to the formation of repulsive forces between the adsorbate on the solid surface and the liquid adsorption rate and uptake capacity of fluoride ions both phase [37]. Therefore, 60 min was taken as the optimum contact time and was used for subsequent experiments.

### 4.3. Effect of pH on adsorption

pH is an important factor controlling the surface charge of the adsorbent and the degree of ionization of the materials in the solution. To determine the optimum pH for the maximum removal of fluoride, the equilibrium sorption of fluoride (with initial fluoride concentration of 100 mg/L) was investigated over a pH range of 2-10.8. Other maintained conditions were: 60 min contact time and adsorbent concentration of 10 g/L. It can be seen in Figure 3 as pH increases the fluoride removal efficiency decreases.



**Figure 3.** Effect of pH on adsorption of fluoride using modified pumice; (initial concentration 100 mg/L, contact time 60 minute and adsorbent dose 0.25g at room temperature)

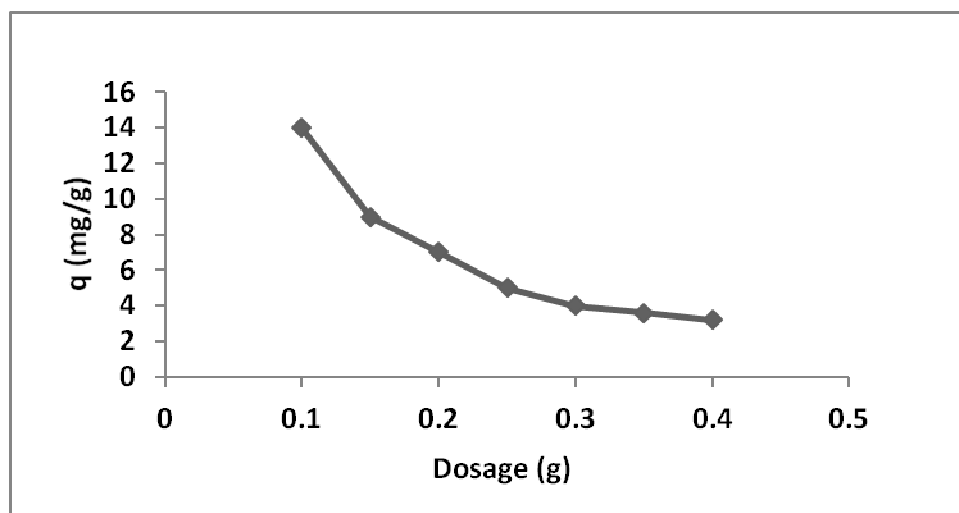
According to the pH, the surface of the adsorbent will be positively or negatively charged.

At higher and lower values pH, the surface of modified pumice will be occupied by  $\text{OH}^-$  and  $\text{H}^+$  ions, respectively [38]. Maximum fluoride removal efficiency (79.6%) and adsorption capacity (7.96 mg/g) were achieved at pH 2. Electrostatic interaction between modified pumice and fluoride molecules in this pH range makes the surface of modified pumice to become positively charged and therefore attracts the negative fluoride anions. The decrease in removal efficiency at pH greater than 2 can be attributed to the competition for the active sites by  $\text{OH}^-$  ions and the electrostatic repulsion of anionic fluoride by the negatively charged modified pumice surface. Similar observations of formation are presented elsewhere [11].

#### 4.4. Effect of adsorbent dosage

The adsorbent dose is an important parameter because it determines the capacity of the adsorbent for a given initial concentration of the adsorbate. The influence of adsorbent of dosage is mainly related to its surface area [39]. It is explained that the more the addition of adsorbent in the solution, the more the availability of active sites for the fluoride binding [24].

The effect of adsorbent dosage on fluoride adsorption using polyaniline modified pumice was studied at different initial doses (0.10-0.4g) by keeping all other parameters constant. It is found that the removal capacity is inversely proportional to dose variations as shown in Figure 4.



**Figure 4.** Effect of adsorbent dosage on adsorption of fluoride using modified pumice; (initial concentration 100 mg/L, contact time 60 minute and pH 2 at room temperature)

In the current study, investigating the effect of adsorbent dosage on the adsorption process made it clear that, as the adsorbent dosage increased from 4 to 16 g/L, the adsorption capacity decreased from 14 to 3.2 mg/g, so that the maximum adsorption capacity on this dose variation was found to be 14 mg/g which was obtained at a smaller dose of 4 g/L due to greater saturation of the adsorbent. In fact, at the initial stage, there were found many empty spaces available to the adsorbate for adsorption [24]. At low dosage (4 g/L) for such adsorbent, all types of sites are entirely exposed for fluoride adsorption and the surface get saturated faster resulting in a higher  $q_e$  value [12]. At higher adsorbent dose (16 g/L), however, the availability of higher energy sites decreases with a large fraction of lower energy sites occupied which results in a lower  $q_e$ .



The dose of modified pumice indicated a decrease in capacity with an increase in adsorbent dose; since the fluoride initial concentration is constant for all doses, it would be distributed over the range of added adsorbent doses; hence fluoride per gram adsorbed would decrease [12]. This observation also agrees well with an increasing solid dose for a fixed solute load as this may result in the availability of fewer fluoride ions per unit mass of polyaniline modified pumice, i.e., lesser fluoride/polyaniline modified pumice ratio with increasing adsorbent dose. Therefore, maximum fluoride removal adsorption capacity (14 mg/g) was achieved at the optimum dose concentration of 4 g/L using polyaniline modified pumice adsorbent.

#### 4.5. Kinetic studies of Adsorption

The kinetic of adsorption system was studied for the determination of how rapidly or deliberately the rate constant of the reaction during the adsorption process. The kinetic data provides valuable information about the effectiveness of the adsorption process. The experimental data were fitted with pseudo first-order and pseudo second-order models.

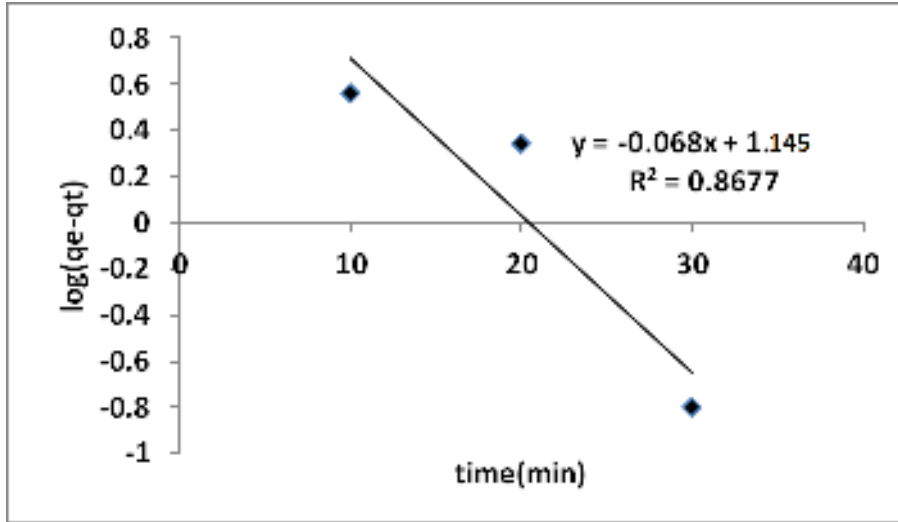
The pseudo first-order equation is generally expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$

Where  $q_e$  and  $q_t$  are adsorbed amounts of fluoride (mg/g) at equilibrium and at time (t), respectively, and  $k_1$  is pseudo-first order rate constant in ( $\text{min}^{-1}$ ). Integrating this equation provides;

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

The pseudo-first order rate parameters were presented in Table 3, where  $k_1$  being calculated from the slope of the graph of  $\log (q_e - q_t)$  versus time t (min). As shown in Table 3 and Figure 5, the adsorption kinetics was not well explained using pseudo-first order kinetics (from observation of  $R^2$  value, 0.867). Moreover, the calculated  $q_e$  (mg/g) values obtained from pseudo first order kinetics did not agree well with the experimental (mg/g) values as shown in Table 3.

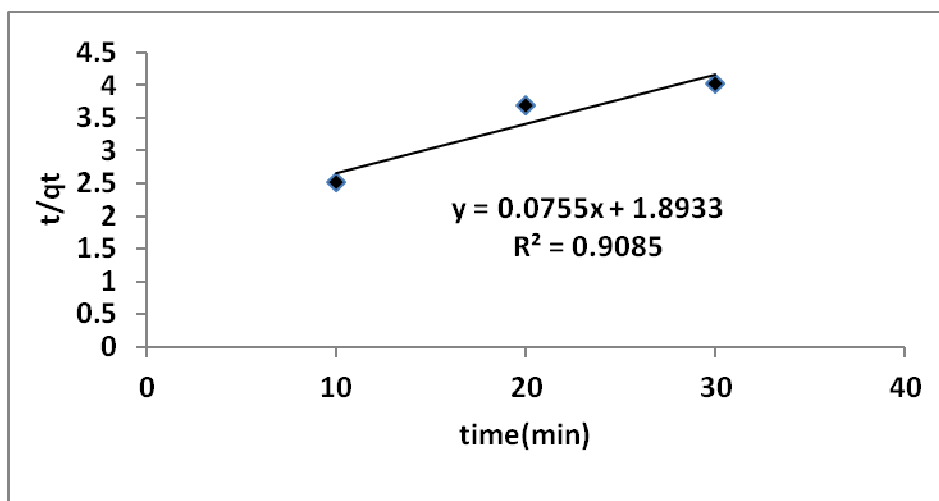


**Figure 5.** Pseudo –first order plot for fluoride adsorption onto polyaniline modified pumice, (fluoride initial 100 mg/L; pH: 2.0 and adsorbent dose concentration 10 g/L at room temperature) The experimental data was also evaluated using pseudo-second order reaction as;

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

Where  $k_2$  is the rate constant (g/mg min). The values of  $k_2$  and  $q_e$  were calculated from the intercept  $\frac{1}{k_2 q_e^2}$  and slope  $\frac{1}{q_e}$  of plot  $\frac{t}{q_t}$  versus  $t$  of (Figure 6) (eq. 4).

Parameters  $q_e$ ,  $q_{e,exp}$ (mg/g), coefficient of determination ( $R^2$ ) and pseudo-second order rate constant  $K_2$  (mg/g min) were reported in Table 3. A high degree of correlation in the experimental data to pseudo-second order equation indicated that adsorption process was governed by chemisorptions processes [40]. Moreover, the calculated  $q_e$  (mg/g) values obtained from Pseudo second order kinetics were in good agreement with the experimental  $q_e$  (mg/g) values (Table 3).



**Figure: 6.** Pseudo –second order plot for fluoride adsorption onto polyaniline modified pumice, (fluoride initial 100 mg/L; pH: 2.0; adsorbent dose concentration 10 g/L at room temperature)

**Table 3.** Kinetic parameters for the adsorption of fluoride using polyaniline modified pumice

Pseudo-first order				Pseudo-second order			
R <sup>2</sup>	q <sub>e,exp</sub> (mg/g)	q <sub>e,cal</sub> (mg/g)	k <sub>1</sub>	R <sup>2</sup>	q <sub>e,exp</sub> (mg/g)	q <sub>e,cal</sub> (mg/g)	k <sub>2</sub>
0.867	7.62	13.96	0.156	0.908	7.62	13.33	0.0029

#### 4.6. Comparison of adsorption capacities of different adsorbents for fluoride removal

An ideal adsorbent that can be used to remove fluoride must have the following characteristics: low-cost, a high fluoride adsorption capacity, rapid adsorption of fluoride and good physical characteristics (rapid water flow without filter clogging). The values of adsorbent capacities of related work have been used for comparison of adsorptive capacities of an adsorbent. Some literature reported values of maximum adsorption capacity, optimum pH and the kinetics that best explained the adsorption process are clearly shown in (Table 4).

**Table 4.** Comparison of adsorption capacities for different adsorbents for fluoride removal.

Adsorbents	Optimum pH	Maximum adsorption capacity qm(mg/g)	References
Natural pumice	3	13.51	[11]
activated carbon prepared coffee	2	0.41	[29]
Calcium materials	3-5	1.07	[41]
MgCl <sub>2</sub> modified pumice	6	5.5	[25]
H <sub>2</sub> O <sub>2</sub> modified pumice	6	11.76	[25]
Polyaniline modified pumice	2	14	Current work

## 5. Conclusions

A batch scale removal of fluoride using adsorptive experiments was performed as a function of solution pH, adsorbent dose, contact time and initial concentration at room temperature. Maximum fluoride removal efficiency was achieved at pH 2, indicated that electrostatic interaction between polyaniline modified pumice and fluoride molecules in this pH range makes the surface of modified pumice to become positively charged and therefore attracts the negative fluoride anions. Fluoride sorption kinetic was fitted to pseudo-second-order model, indicated that adsorption process was governed by chemisorption processes. The maximum uptake of fluoride was found to be 14 mg/g, indicating the promising nature of polyaniline for fluoride removal.

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