DEVELOPMENT OF AN ADSORBENT MATERIAL TO REMOVE FLUORIDE FROM WATER

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ABSTRACT

Groundwater is a scarce commodity in Sri Lanka where it fulfills more than 80% of rural drinking water supply-demand. Dental fluorosis, skeletal fluorosis, and kidney diseases are commonly observed in most parts of rural areas due to the presence of fluoride in groundwater at harmful levels (>1mg/L). The conventional water treatment process has failed to ensure safety level of fluoride in water before consumption. Adsorption is one of the widely used methods of removing fluoride due to its effectiveness, low cost and availability of wide range of adsorbents. Chitosan is a low-cost biopolymer used as a biosorbent for fluoride removal. In this study, chitosan-activated sawdust composite beads were prepared to compare its effectiveness against raw chitosan in removal of fluoride from synthetic fluoride solution. Chitosan and activated sawdust were converted into bead form and they were chemically modified via crosslinking followed by protonation. The effect of adsorbent dosage, initial fluoride concentration and contact time were investigated by conducting batch experiments in neutral pH at room temperature. Fluoride sorption equilibrium was reached after 1 hour for modified chitosan with excellent removal efficiency more than 90% whereas raw chitosan indicated a very low removal efficiency of 16% after 2 hours of reaching the equilibrium. At 90% removal, the final fluoride content was recorded at 0.5mg/L and it is well below 1mg/L which is required as per Sri Lankan Standards for Potable Water (SLS 614:2013). Langmuir and Freundlich isotherm models were adopted to understand the mechanism of adsorption and Langmuir model was found to be fit well with experimental data. The maximum adsorption capacity according to Langmuir was found to be 4.413 mg/g. The kinetics of the sorption process followed pseudo second order model. Considering above facts, the developed sorbent material gives promising results in removing fluoride from water.

Keywords: Chitosan; Adsorption; Fluoride; Composite; Crosslinking; Beads

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LIST OF ABBREVIATIONS

ACCCB	Activated Carbon Chitosan Composite Beads
C_0	Initial Concentration of Adsorbate
CAC	Chitosan -Activated Carbon
C_e	Equilibrium Concentration of the Adsorbate
Ce-SGCS	Cerium loaded Silica Gel Chitosan
C_i	Initial concentration of adsorbate
CKDu	Chronic Kidney Disease of unknown etiology
d	Inter planer distance of the lattices
E (%)	Removal efficiency
EDX	Electron Dispersive X-ray
FTIR	Fourier Transform Infrared Spectroscopy
k_1	Rate constant of pseudo-first-order adsorption.
k_2	Rate constant of pseudo-second-order adsorption
k_a	Langmuir isotherm constant.
k_f	Freundlich isotherm constant (mg/g) related to adsorption
N	Avogadro’s number
NWS&DB	National Water Supply and Drainage Board

PCCB	Protonated Cum Carboxylated Beads
pHzpc	Zero Point Charge
PSCCB	Protonated Sawdust Chitosan Composite Beads
q_e	Adsorption capacity at equilibrium
q_m	Maximum monolayer sorption capacity
q_t	Adsorption capacities at time t
R^2	The correlation coefficient
R_L	The nature of the adsorption process
RO	Reverse Osmosis
SCCB	Sawdust Chitosan Composite Beads
SEM	Scanning Electron Microscopy
SGCS	Silica Gel Chitosan
SLS	Sri Lankan Standards
V	Volume of solution
W	Weight of the adsorbent added
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background

Water scarcity is becoming a growing concern in the world with limited access to safe water supply sources. In context of Sri Lanka, the rural community, especially in dry zone of the island, face the scarcity of water and they mostly depend upon ground water for domestic use. However, the quality of ground water in Dry Zone of Sri Lanka remains in question as there is no proper way of treating groundwater before consumption.

The quality of groundwater plays a major role in aspect of health and it must be ensured that it is free of any disease causing contaminants. Researchers have found out that the presence of chemical contaminants in ground water of Sri Lanka, have exceeded their permissible limits (Dissanayake, 2010). Among several biological and chemical impurities, abundance of fluoride in groundwater is a major concern particularly in dry zone of the country. Due to high intake of fluoride rich water, several health problems such as dental caries, dental fluorosis and skeletal fluorosis has been reported in the rural community over the past years. (Dissanayake, 2010). Even though, WHO standard states , 0.5-1.5 mg/l is the safe level for fluoride where it actually promotes dental health, SLS 614:2013 standard gives an upper limit of 1.0 mg/l for Sri Lanka since it is a tropical country and due to high consumption of water. According to Chandrajith, et al. (2012), the cause for excessive presence of fluoride in groundwater is weathering of fluoride bearing minerals such as Biotite, Hornblende, Pyroxene, Sphene, and Apatite, and also application of fluoride containing fertilizer in agricultural activities.

Fluoride does not affect taste, colour or smell of water. Therefore concentrations cannot be identified unless tested in laboratory. There are several technologies adopted to remove fluoride from water such as coagulation and precipitation, membrane processes, electrochemical treatments and ion-exchange. Even though these methods have proven to be highly effective they are expensive and demand high capital, running and maintenance costs.

Therefore, the focus has been given to the method of adsorption which has been widely studied over recent years and has become more popular due to several advantages like low cost, greater accessibility and availability of wide range of adsorbents (Stanic, et al 2014).

Adsorption is a separation process where molecules tend to concentrate on the surface of the adsorbent as a result of Van der Waals force or chemical bonds which exists between the molecules. Factors that affect adsorption are temperature, surface area of adsorbent, initial pH of medium, adsorbent dosage, contact time, porosity etc. A wide range of adsorbents and their modifications have been tested for the removal of fluoride from water such as oxides and hydroxides (iron oxides, titanium oxides etc.), geomaterials (saw dust, ground nut husk, zeolite etc.), carbonaceous materials like activated carbon , industrial products and by products (bone char, wastemud, fly ash, aluminium salt) and biosorbents (Stanic, et al., 2014).

However, uses of biosorbents for fluoride removal provide several advantages over other adsorbents like biodegradability, biocompatibility, safe and non-toxity and abundance in nature. Various biosorbents have been studied for removal of fluoride and some of them are algal biosorbents, waste fungus biosorbents, bone char sorghum, canola and chitosan. In recent years, numerous studies have aimed to develop cheaper and more effective natural polymer adsorbents and out of them, chitosan is considered to be one of the most promising and applicable materials in adsorption applications.

Chitosan is a naturally occurring abundant biopolymer produced commercially by deacetylation of chitin under alkaline conditions. This low cost adsorbent is biodegradative, environmentally friendly, and nontoxic and occurs naturally in the form of flakes or powder. However, to overcome its limited adsorption capacity due to low porosity, low surface area and low mechanical strength, conversion of chitosan into bead form and adopting several chemical and physical modifications have been widely investigated by the researchers (Agarwal,et al.,2017; Miretzky, et al.,2011). Presence of functional groups such as –OH and $-NH_2$ facilitates the chemical modification of chitosan and increases its adsorption capacity. Out of several chemical modifications such as grafting, crosslinking, chelation and protonation, crosslinking followed by protonation has provided with the most promising results in defluoridation (Younes, et al., 2015).

Further to chemical modifications, a large amount of research has also been focused on the preparation of composite beads in removal of fluoride with numerous materials like metals, metal oxides and biochar. Studies show that modified chitosan has proven to be more effective than raw material.

1.2 Objectives

Objectives of this study are,

- To develop a novel chitosan based adsorbent material.
- To analyze the efficiency of raw and modified chitosan adsorbents in removing fluoride from synthetic fluoride solution.

1.3 Scope

- Develop a novel chitosan based adsorbent material to analyze the removal efficiency of F^- from synthetic F^- solution.
- The characterization of raw and modified chitosan adsorbent by pH of zero point charge (pH_{zpc}) method.
- Investigating the effect of contact time, adsorbent dosage, and initial fluoride concentration on the removal efficiency.
- Conduct adsorption kinetics and isotherm studies.
- The experiments were conducted at neutral pH and effect of pH on removal efficiency is not under the scope of this study since groundwater is considered to be at neutral pH.
- The research was limited to batch experiments, and column tests are outside the scope of this study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the water quality and ground water related issues in Sri Lanka due to high concentrations of fluoride. Fluoride removal methods and chitosan modification for fluoride removal will be further reviewed. Moreover, characterization methods of modified adsorbent, isotherm and kinetic studies for the adsorbent will be reviewed through this chapter.

2.2 Groundwater quality issues in Sri Lanka

Sri Lanka being a country in the tropical region of the world, consumption of water is higher in the dry zone of the country where water is a scarce commodity and relies on groundwater sources rather than surface water.

Groundwater is believed to be comparatively much clean than surface water, but several anthropogenic activities as well as natural phenomenon aforementioned in the introduction have caused contamination of groundwater where treatment is needed before consumption. According to the recent studies up to 85 percent of the rural drinking water supply needs are met from groundwater (Panabokke, et al., 2007), thus groundwater has an important bearing on the health of the people. Presence of contaminants exceeding their permissible limits will create several health problems to the consumers. Previous researches have confirmed high concentrations of nitrates, fluorides, chlorides, sulphates, heavy metals like iron, arsenic, manganese, and hardness can be found in groundwater. Fluoride is a negatively charged ion and one of the most geochemically and biochemically reactive element which makes it detrimental to health when consumed in excessive amounts. Researchers conducted in the recent past have discovered that high concentration of fluoride is present in groundwater particularly in the dry zone of the country. A spatial distribution map of groundwater fluoride levels prepared using nearly 14000 groundwater fluoride data provide clear evidence regarding this matter (Chandrajith,et al., 2012).

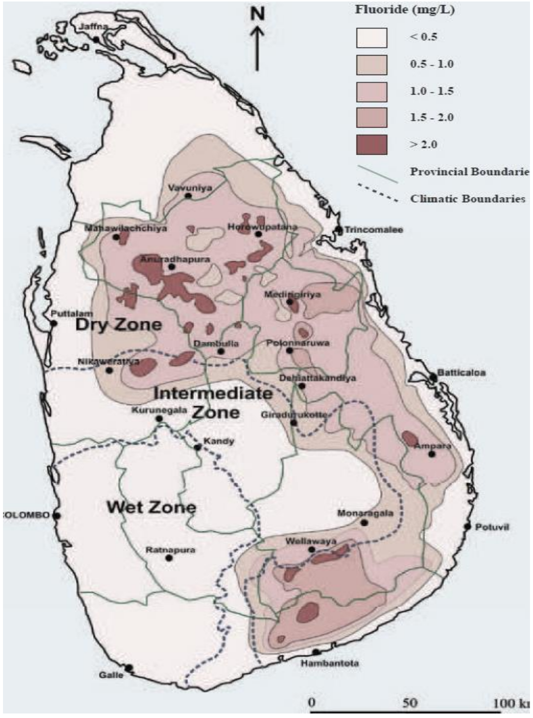

Figure 2.1 The distribution of fluoride in groundwater in Sri Lanka (Chandrajith, et al., 2012)

According to the studies, over 25% of wells have fluoride exceeding 2 ppm ,whereas in some areas the level has exceeded 10 ppm as well (Dissanayake, 2010). The reason that the presence of high fluoride levels is a unique feature of the dry zone is the climate and the hydrological conditions such as high evapotranspiration and slow rate of groundwater movement in these low plains (Dharmagunawardhane,2009;Chandrajith, et al.,2012).As per WHO standards the safe level of fluoride is set at 0.5-1.5 ppm where it actually promotes dental health and any levels beyond these limits will result in dental fluorosis, skeletal fluorosis and crippling fluorosis, whereas dental caries , limited growth and fertility problems occur when it is not taken at required levels(WHO,2011). According to a National Oral Health Survey report in 2002-2003, the prevalence of dental fluorosis in Sri Lanka among 12-year-old children ranged between 0-71% with the highest being reported in Anuradapura (71%), Matale (55%), Hambantota (38%), Polonnaruwa (32%), Kurunegala (27%), Vavuniya (26%), Moneragala (21%), Ampara (19%) and Rathnapura (18%) (Ranasinghe, et al., 2018). In addition to this the chronic kidney disease of unknown etiology (CKDu) has become controversial for the past two decades in the country and several researchers have identified fluoride as a probable risk factor for this disease **(**Dissanayake, et al., 2017).

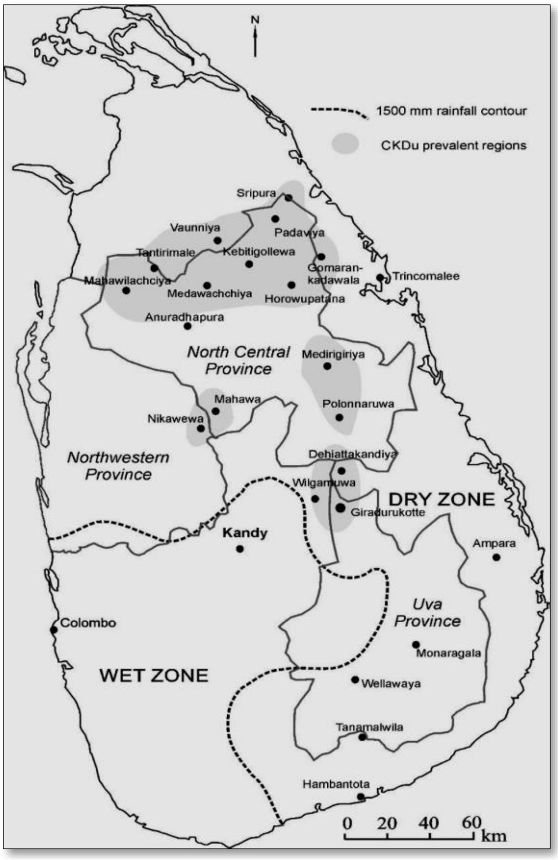

Figure 2.2 Distribution of Chronic Kidney Diseases with uncertain etiology (CKDu) in the dry zone of Sri Lanka (Dissanayake, et al., 2017)

Even though no definitive cause has been identified for this disease, previous research has found an association with for the prevalence of CKDu with farming occupation where farmers in the rural area, peculiarly in the agricultural-based communities work long hours in hot and humid conditions and at the same time, consume a lot of fluoride-rich water. A recent population-based cross-sectional study has estimated the point prevalence of CKDu between 15.1 and 22.9 % in predominant agricultural areas of Anuradhapura, Polonnaruwa, and Badulla (Rajapaksa, et al., 2016). Due to the high consumption of water, the standard level of fluoride is 1mg/L being the upper limit as per Sri Lankan potable water standard (SLS 614:2013) while, 0.5-1.5 mg/Lis the safe level recognized by the WHO standard. Since the rural community of the country mostly depend on groundwater for their domestic purposes and due to the lack of known treatment for fluorosis and other health hazards it is vital to ensure the safe level of fluoride before consumption. As fluoride does not alter water color taste or the odour, the concentration could be identified only by carrying out a laboratory test (Dharmagunawardhane, 2009).

2.3 Removal methods of fluoride from water

A number of water treatment technologies have been implemented worldwide to remove fluoride from water and bring water up to the drinking water standard. Reverse Osmosis, Ion Exchange and the Adsorption Technologies are the mostly adopted technologies for fluoride removal.

Ion exchange processes are reversible chemical reactions for removing dissolved ions from solution and replacing them with other similarly charged ions. In anion exchange resins, fluoride ion substitute chloride ions on resin surface. When the resin is exhausted, it could be regenerated by backwashing with supersaturated water with dissolved sodium chloride (Waghmare, 2015). The restrictions of this process are high cost, pH of treated water being low and presence of high concentration of chloride, possible organic and bacterial contamination from resins (Kansara, et al., 2016).

Reverse Osmosis is a physical process in which the anions are removed by applying pressure on the feed water where it gets directed through a semi permeable membrane (Waghmare, 2015). Reverse Osmosis membrane rejects ions based on size and electrical charge. Efficiency of the process is mainly governed by factors such as raw water characteristics, pressure, temperature and regular monitoring and maintenance (Singh, et al.,2016). However main drawbacks of this technology includes requirement of pretreatment in order to protect the membranes from obstruction of pores, high cost and requirement of post treatment for remineralization (Waghmare,2015).

Apart from these expensive methods, nowadays more focus has been given to the adsorption technology specially in the developing countries due to its cost effectiveness, easy operation, availability of wide range of adsorbents and environmental friendliness. Adsorption process is a surface phenomenon where particles/pollutants get adhered on to a solid surface. Particles which stick to the solid surface are called adsorbate while the solid surface is called the adsorbent (Ali and Gupta, 2006). Depending upon the nature of forces existing between adsorbate molecules and adsorbent, the adsorption can be categorized into two types: namely, Physical adsorption/physisorption and chemical adsorption/chemisorption.

In physical adsorption the adsorbate and adsorbent are held together by weaker Van der Waal forces, where in chemical adsorption there is a formation of chemical bond by sharing of electrons thereby making the force of attraction very strong. Generally physical adsorption is reversible but chemical adsorption cannot be easily reversed.

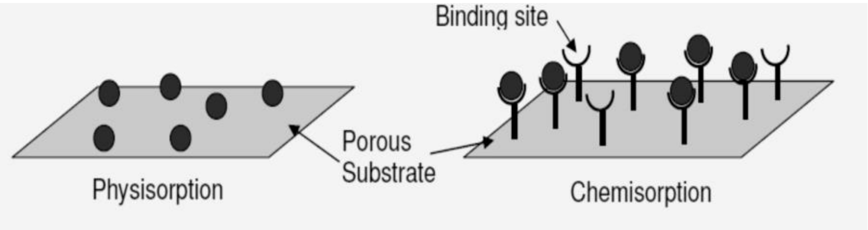

Figure 2.3 Physisorption and chemisorption processes **(**Berger &Bhown, 2011)

The adsorption depends on several factors such as temperature, pressure, surface area of the adsorbent, pH, contact time, pore volume and also concentration of the adsorbate (Worch, 2012). One of the major fact that the adsorption process is now widely studied is the availability of wide range of adsorbents. A variety of adsorbents and their modifications have been studied for defluoridation (activated carbons, activated, bauxite, hematite, polymeric resins, activated rice husk, brick powder, red soil, charcoal, brick, fly ash, granular ceramics, chitosan, modified ferric oxide/hydroxide, hydroxyapatite (HAP), zirconium and cerium modified materials, titanium-derived adsorbent, clays, zeolite and magnesium-modified sorbents). Out of these activated carbon is the most widely used adsorbent for water treatment due to existence of high surface area and pore volume (Stanic, et al., 2014). Among these different kinds of adsorbents, use of biosorbents has been trending in the recent past due to the abundance of biomaterials and several other factors such as environmental friendliness, low cost, non-toxicity and biocompatibility. Many biomaterials such as rice husk, saw dust, bone char and chitosan has been investigated for biosorption studies (Stanic et al, 2014).

2.4 Chitosan

Chitosan has become one of the widely studied biosorbent because of its unique properties such as biodegradability, biocompatibility and low cost. In addition to this the presence of functional groups such as hydroxyl (-OH) and amine (-NH2) has provided the ability to chemically and physically modify this polymer (Stanic, et al., 2014). Chitosan is derived from deacetylation of chitin present in the exoskeletons of shellfish. In this deacetylation process the acetyl groups of chitin get converted into free amine groups and this step determines the degree of deacetylation or ratio of deacetylated to acetylated groups. Amine groups act as major functional groups in chitosan (Valkili, et al.,2014).

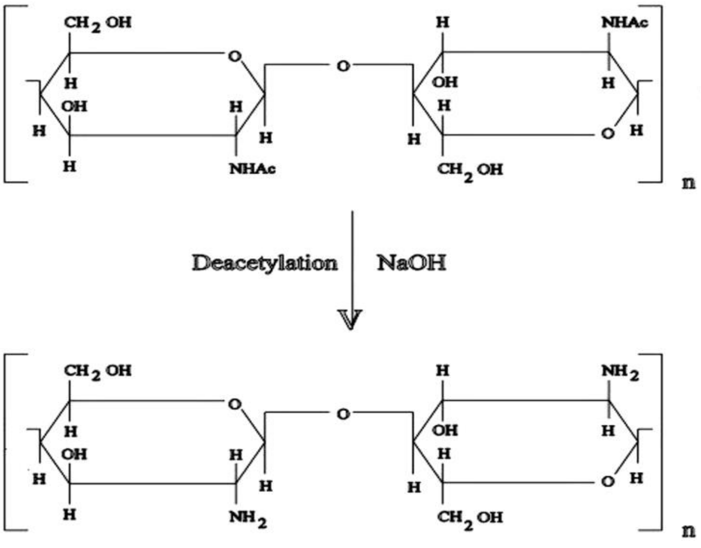

Figure 2.4 Deacetylation of chitin into Chitosan(Agarwal,et al.,2017)

Throughout the literature, raw and modified chitosan has been investigated as an adsorbent for removal of reactive synthetic dyes such as Congo red, Acid violet. Acid orange and Heavy metals such as As(III), Cr(VI), Cu(II), Cd(II), Pb(II), organic matter and also fluoride from water. Physical and chemical modifications have been implemented on chitosan since the raw material exhibits poor adsorption capacity due to low porosity, low surface area, low acid stability, and low thermal stability (Valkili, et al., 2014; Ngah, et al., 2011). These modifications mainly include crosslinking grafting, protonation and chelation

2.4.1 Chitosan as an adsorbent for fluoride removal

In literature it is rarely found that raw chitosan is used for defluoridation. Chitosan has the ability of forming gels and hydrogel networks, polymeric resins, beads, membranes, fibers or composite materials and therefore more focus has been given to these modified forms of chitosan (Agarwal, et al., 2017).

Since this raw material exhibits low adsorption capacity they have been transformed into bead form to increase surface area, porosity, and improve access to internal adsorption sites and widely studied in context of fluoride removal (Vakili,et al., 2014). These chitosan beads have been chemically modified through cross linking, grafting and protonation as well. Since chitosan undergo dissolution in at lower pH it severely limit the use of chitosan as an adsorbent and to overcome this it has been modified via crosslinking the polymer chains through cross linking agents such as Glutaraldehyde, Epichlorohydrin, Tripolyphosphate etc. (Vakili et al., 2014). Figure 2.5 depicts the process of crosslinking chitosan with glutaraldehyde which severely increases its mechanical strength thus making it insoluble in acidic media.

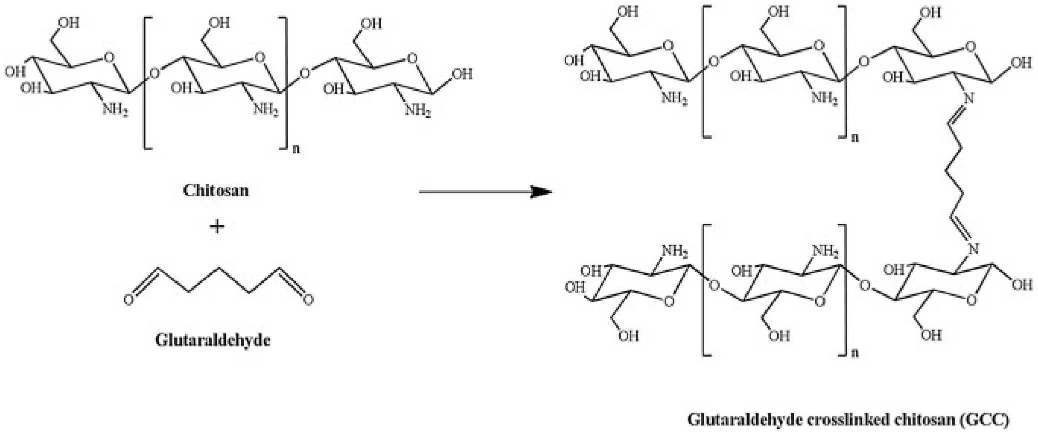

Figure 2.5 Glutaraldehyde Cross-Linked Chitosan Copolymer Resin (Nagiredd, et al., 2017)

Vishwanathan, et al., (2009) has prepared protonated cum carboxylated cross-linked chitosan beads where beads were crosslinked with glutaraldehyde prior to protonation of both amine and hydroxyl groups, treating with chloroacetic acid followed by hydrochloric acid. Further it is reported that fluoride removal occurs via hydrogen bonding.

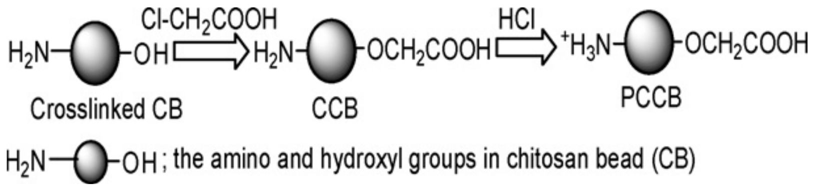

Figure 2.6 Synthesis of PCCB Resin (Vishwanathan,et al.,2009)

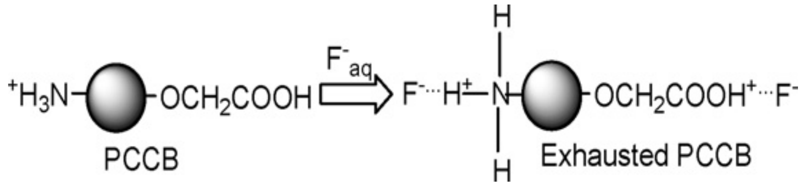

Figure 2.7 Mechanism of fluoride sorption by PCCB (Vishwanathan, et al., 2009)

Moreover, the metal binding property of chitosan has been incorporated in the process of defluoridation. Ammine functional group will donate its lone pair of electrons with metal ions to form polymer ion complexes. Vishvanathan and Meenakshi (2008) made use of this mechanism by incorporating Fe^{3+} ion to form Fe^{3+} loaded carboxylated chitosan beads (Fe-CCB) and obtained successful results.

Apart from chemical modification of chitosan, a large number of researches have focused on the preparation of composites of chitosan with numerous materials such as metals, metal oxides and biochar for fluoride removal. Jagtap et al.,(2009) has incorporated titanium metal to upgrade the fluoride removal capacity. Bansiwal et al.,(2009) utilized lanthanum incorporated chitosan beads for removal of fluoride from water. Sundaram et al., (2009) has prepared biocompatible Nano-hydroxyapatite/chitin composite for defluoridation. The experimental data fitted well with Freundlich and Langmuir isotherm models. Sundaram et al., (2009) have utilized magnesia-chitosan composite (MgOC) prepared by mixing magnesium oxide and chitosan. Effects of adsorbent dosage, initial fluoride concentration and contact time have been investigated. The equilibrium and kinetic studies were carried out with Freundlich isotherm and pseudo-second-order kinetic model. FTIR and SEM with EDX studies have been performed to characterize the composite. Viswanathan et al., (2010) utilized alumina-chitosan composite in his experiments for defluoridation of water. The influence of contact time, pH and presence of other anions were investigated. The characterization of the sorbent had been performed by FTIR, AFM and SEM with EDX analysis.

Prabhu and Meenakshi (2014) prepared silica gel/chitosan (SGCS) and cerium loaded silica gel/chitosan (Ce-SGCS) composites for sorption studies. The influences of various parameters like contact time, pH and adsorbent dosage on defluoridation capacity of the sorbents has been investigated. FTIR, SEM with EDX and XRD studies has been performed to characterize the composite. The two main types of sorption kinetic models, namely reaction-based and diffusion-based models, were adopted to fit the experimental data. Langmuir, Freundlich isotherms were used to quantify the sorption capacities.

Among the adsorbent materials available activated carbon is considered one of the most used adsorbent worldwide since it has high surface area and high pore volume. Organic material with higher carbon content such as coal, peat, wood, coconut shells could be used as raw material for activated carbon. It binds the materials by Van der Waals forces (kaur,2013). In studies of using activated carbon for fluoride removal it has been modified by oxidation and subsequent impregnation with high valent ions such as Zirconium, Titanium, Iron, and Calcium etc. Oxidation has been carried out to introduce Carbon-Oxygen surface groups in Activated Carbon. They have utilized oxidizing gases (Oxygen, Steam, Carbon etc.) or oxidizing solutions (Nitric Acid, Hydrogen Peroxide, Chlorine Water etc.).

Activated carbon prepared by pyrolysis of rice straw at 550, 650 and 750 °C were modified by liquid-phase oxidation using HNO_3, H_2O_2 and $KMnO_4$ and fluoride removal was investigated by Daifullah et al,(2007). The authors have reported that the best results and

100% of fluoride removal was obtained with activated carbons oxidized with $KMnO_4$ (Stanic et al, 2014). There are several reported literature on use of biochar for fluoride removal such as activated sawdust, pine wood char, activated rice husk and slow pyrolysis orange peel char, where they have obtained satisfying results on fluoride removal (Mohan, et al., 2014). However, chitosan activated carbon composites have not been studied for defluoridation.

2.4.2 Preparation of chitosan beads and effect of influencing parameters for defluoridation

Throughout the literature it could be found that for the preparation of beads initially, chitosan is dissolved in acetic acid and then added dropwise into sodium hydroxide solution. Zhao et al., (2006) has explained this phenomenon in preparation of chitosan gel beads for copper (II) adsorption. When chitosan is dissolved in acetic acid NH2 groups get protonated and when injected drop wise into aqueous solution of NaOH it reacted with both protonated amine groups and acetic acid within chitosan solution where liquid-liquid phase separation occurred and the chitosan gel was coagulated to form porous spherical uniform chitosan gel beads. Vishwanathan et al, 2008 followed the same procedure by dissolving Chitosan (20 g) in 2.0% glacial acetic acid solution (1000 ml) and dropping into a 0.5M aqueous NaOH solution to form uniform chitosan beads in process of removing fluoride from aqueous solutions. Vakili et al., (2014) in his study on adsorption of reactive blue 4 using chitosan beads observed that increase in acetic acid concentration beyond 1wt% showed lower adsorption capacities due to depolymerization and deformation in pore network and also chitosan concentration beyond 2wt% dye removal decreased due to increase in intermolecular entanglement of chitosan chains and consequently decreased the accessibility of dyes to adsorption sites, thus 2wt% chitosan and 1wt% acetic acid was identified as optimum for adsorption.

In the study of influencing parameters for defluoridation mainly the effect of initial fluoride concentration, contact time, adsorbent dosage and pH has been evaluated by Meenakshi et al., (2008) and it is depicted in figure 2.8. Vishvanathan and Meenakshi (2008) conducted a similar experiment incorporating Fe-CCB and arrived at similar behavior when investigated for above parameters.

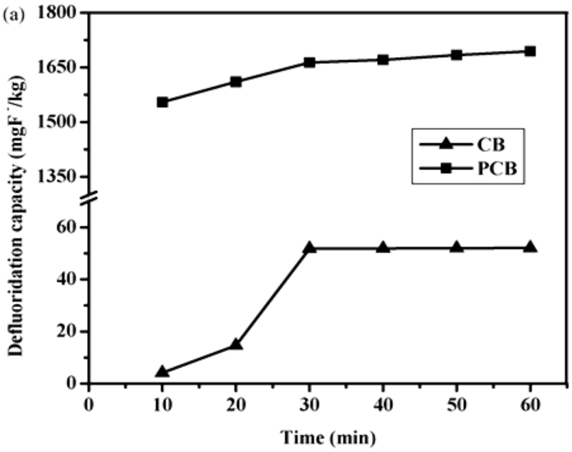

Figure 2.8 Effect of contact time on fluoride removal (Meenakshi, et al.,2008)

Meenakshi et al., (2008) has observed that adsorption on both raw and modified adsorbents increases with contact time and reaches a level of equilibrium and it is depicted in figure 2.9. Many of the other researches also support this observation. The time which the adsorption equilibrium is attained is known as the equilibrium time and it is independent of the initial fluoride concentration (Xu, et al., 2011).

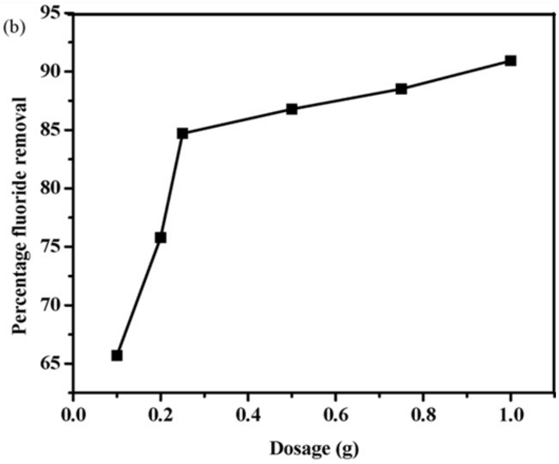

Figure 2.9 Effect of adsorbent dosage on fluoride removal (Meenakshi, et al., 2008)

The effect of adsorbent dosage has been investigated in the literature and it is reported that percentage removal of fluoride increased with increase in sorbent dosage in most cases. Meenakshi et al., (2008) further explained these phenomena as number of active sorption sites increases when dosage increase (figure 2.9) Defluoridation experiments conducted by Vishvanathan and Meenakshi (2008) also provide proof for this statement.

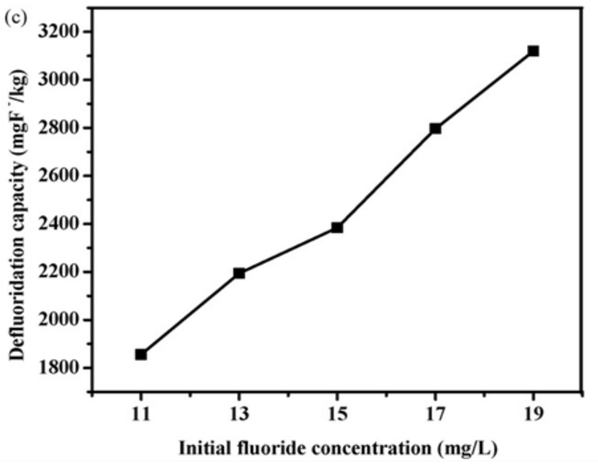

Figure 2.10 Effect of initial fluoride concentration on fluoride removal
(Meenakshi, et al., 2008)

Initial fluoride concentration is one of the most important parameter affecting the adsorption process. In the study conducted by Meenakshi, et al.,2008, adsorption capacity increased dramatically with the increase in initial fluoride concentration (Figure 2.10) Patnaik, et al.,(2016) states the reason for this behavior as higher concentration gradient acting as a driving force to overcome mass transfer resistance between bulk solution and adsorbent surface. It is evident that removal capacity increases with time, dosage and initial concentration of fluoride.

2.5 Adsorption equilibrium study

Adsorption equilibrium studies are used to describe the relation between equilibrium concentration of adsorbate and amount adsorbed at equilibrium (Worch, 2012). Parameters and constants in these equations helps to understand the interactions of adsorbate and adsorbent, evaluate maximum adsorption capacities as well as the adsorption mechanism.

2.5.1 Langmuir isotherm

Langmuir adsorption isotherm model assumes monolayer adsorption with adsorption can only occur at a finite number of definite localized sites, which are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In this isotherm model there is an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place. (Foo, et al., 2010)

Langmuir isotherm has been successfully proven for many adsorption processes. It is widely adopted in fluoride removal studies as well. It depends on several assumptions including,

- The energy is equally distributed over the adsorbent surface
- Contaminant molecules gets adsorbed on specific sites and will not migrate over the surface
- The adsorption will take place in the monolayer surface of the adsorbent material and
- Adsorbent molecules will not interact with each other. (Annaduzzaman, 2015)

This method has been widely used to describe the adsorption mechanism of the adsorbent materials. The Langmuir isotherm model can be given by the following equation:

$$q_e = \frac{q_m k_a C_e}{1 + k_a C_e}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_a} \frac{1}{C_e}$$

Where q_e(mg/g) is adsorption capacity at equilibrium, C_e (mg/l) is equilibrium concentration of the adsorbate, q_m (mg/g) maximum monolayer sorption capacity, and k_a (L/mg) is the Langmuir isotherm constant.

$$R_L = \frac{1}{1 + k_a C_i}$$

Where C_i is the initial concentration of adsorbate in mg/l. R_L indicates the nature of the adsorption process, as given below:

- $R_L > 1$ Unfavorable
- $R_L = 1$ Linear
- $0 < R_L < 1$ Favorable
- $R_L = 0$ Irreversible

2.5.2 Freundlich isotherm

Freundlich isotherm is used to describe a non-linear sorption process. This is applicable for adsorption processes occurring on heterogonous surfaces. It is also used to describe the multilayer sorption mechanism. It gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies (Ayawei,et al., 2017). Freundlich model can be expressed by following equation.

$$q_e = k_f C_e^{1/n}$$

$$log q_e = log k_f + \frac{log C_e}{n}$$

Where q_e (mg/g) is adsorption capacity at equilibrium, C_e (mg/l) is equilibrium concentration of the adsorbate, k_f (mg/g) Freundlich isotherm constant (mg/g) related to adsorption capacity and n is the adsorption intensity. n indicates the nature of the adsorption process, as given below (Aljeboree, et al., 2014).

- n = 1 adsorption is linear

- n < 1 adsorption process is chemical

- 1< n < 10 adsorption is a favorable physical process

2.6 Adsorption Kinetic Studies

Adsorption kinetics is a measure of adsorption uptake with respect to time at a constant concentration and it is employed to measure the diffusion of adsorbate in the pores. Here a solute volume is brought to contact with the adsorbent and the resulting change of concentration with time is measured (Worch, 2012).

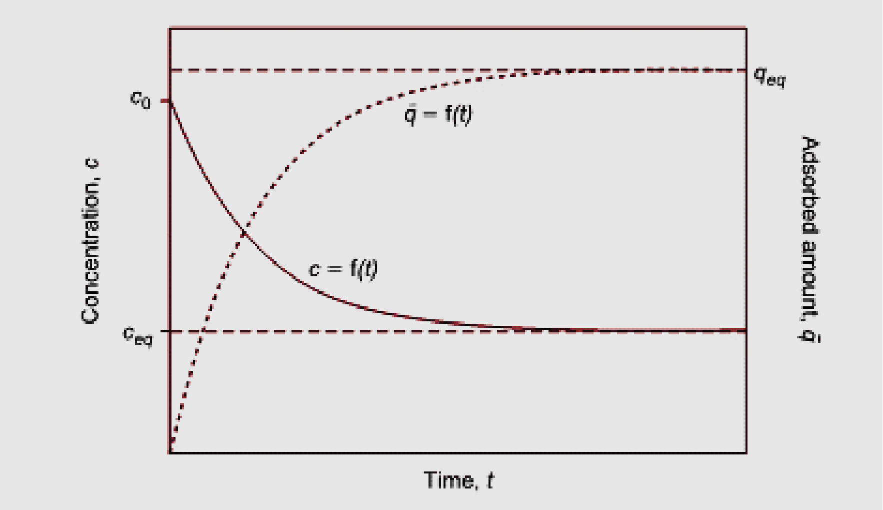

Figure 2.11 Resulting change of concentration with time (Worch, et al., 2012)

2.6.1 Pseudo-first-order kinetics

It is believed to be one of the earliest model regarding adsorption. It is used in many fluoride removal studies and can be presented as follows.

$$\mathrm{q}_t = q_e(1 - e^{-k_1 t})$$

$$\ln(q_e - q_t) = lnq_e - k_1 t$$

Where q_e (mg/g) is adsorption capacity at equilibrium, q_t (mg/g) is adsorption capacities at time t, k_1 (1/min) is the rate constant of pseudo-first-order adsorption. (Worch, et al., 2012)

2.6.2 Pseudo-second-order-model

It is very similar to first order model where the uptake is governed by second order rate equation.

$$\mathrm{q}_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

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

Where q_e (mg/g) is adsorption capacity at equilibrium, q_t (mg/g) is adsorption capacities at time t, k_2 (g/mg/min) is the rate constant of pseudo-second-order adsorption (Worch, et al., 2012)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Summary of methodology

Figure 3.1 shows the summary of the methodology.

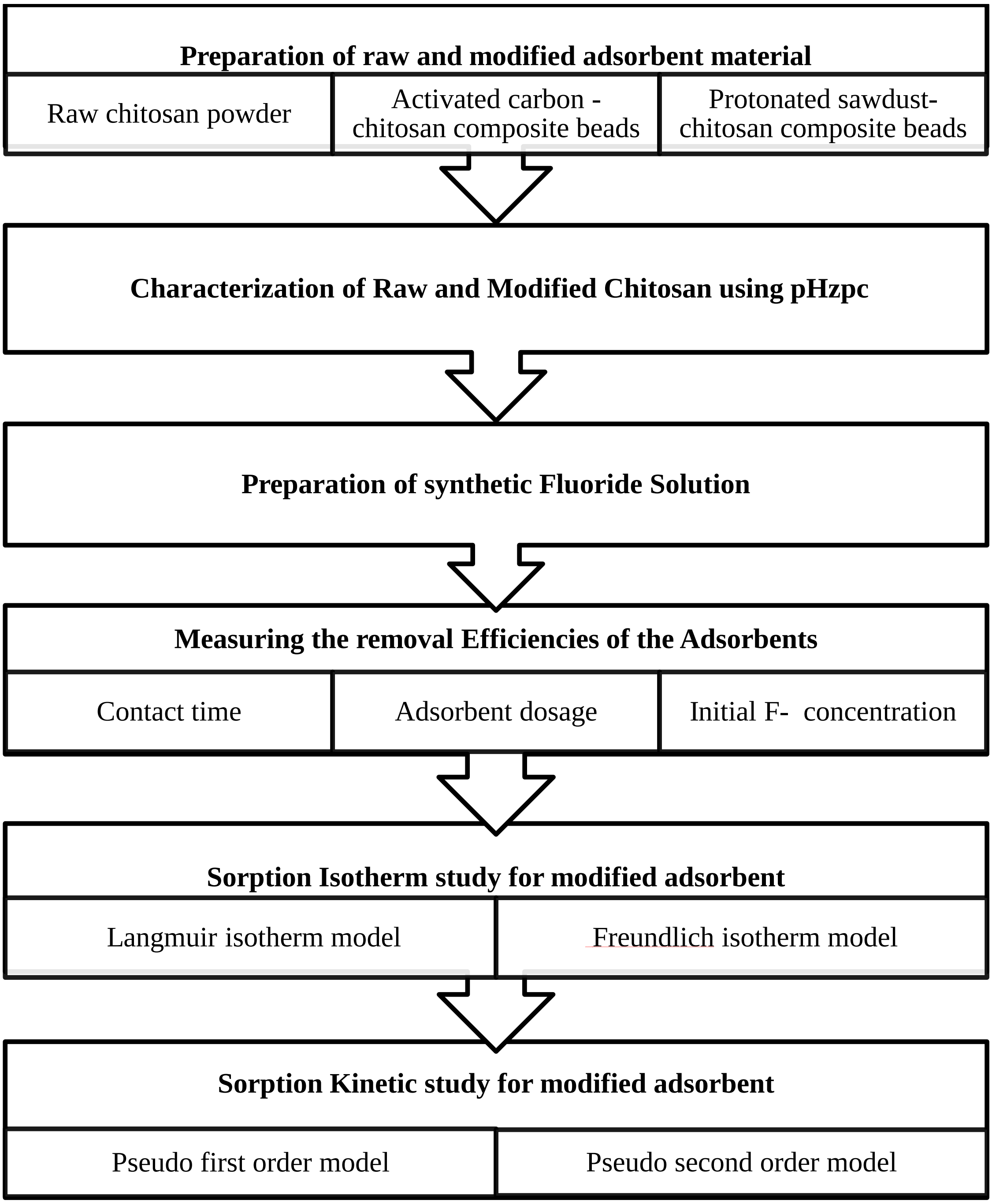

Figure 3.1 Summary of Methodology

3.2 Materials

Chitosan powder obtained from Norwegian University of Life Sciences was used as the raw material. Physical modification of chitosan was carried out using Acetic acid (1 % (v/v) CH_3COOH), Sodium Hydroxide, Powdered Activated Carbon obtained from Sisco Research Laboratories Pvt. Ltd, India and Pyrolyzed Sawdust Prepared from softwood Sawdust (550^0-650^0). Anhydrous sodium fluoride (NaF) used to prepare the synthetic fluoride solution. Crosslinking of chitosan beads was carried out using Glutaraldehyde solution (Grade II, 25% in H_2O). Concentrated Hydrochloric acid (HCl) was used for the protonation of the beads. Hydrochloric (HCl) and sodium hydroxide (NaOH) solutions were used for pH adjustments in all experiments. HACH fluoride SPADNS reagent was used to measure the fluoride concentration.

3.3 Preparation of adsorbent materials

Initially, Activated Carbon Chitosan Composite Beads (ACCCB) were prepared. Then, the removal efficiency was investigated for ACCCB and it was observed that the beads were not performing to the required removal efficiency. Subsequently, Sawdust powder was mixed with Chitosan powder to produce Sawdust Chitosan Composite Beads (SCCB). The removal efficiency of SCCB was higher than ACCCB. However, it was found that SCCB performance could be further enhanced by chemical modification. Therefore, Protonated Sawdust chitosan composite beads (PSCCB) were prepared.

3.3.1 Preparation of raw adsorbent

Raw chitosan powder was used without any pretreatment as the raw adsorbent material.

3.3.2 Preparation of Activated carbon -chitosan composite beads

To prepare activated carbon based chitosan composite beads; first the chitosan solution was prepared by dissolving 3g of chitosan powder into 100 ml of 1.0% (v/v) acetic acid solution. Then, the powdered activated carbon 1 g was added to the solution and stirred using magnetic stirrer for 3h at room temperature. After mixing, the solution was added drop wise to 2.0 M Sodium Hydroxide solution through a syringe, at a constant rate to prepare composite beads. The beads were kept in the NaOH solution for 24 h. Then, the wet composite beads were washed with distilled water until constant pH is reached. Finally, the beads were dried at room temperature and used for sorption studies (Vishvanathan, et al., 2009).

3.3.3 Preparation Sawdust- chitosan composite beads

To prepare Sawdust powder first, pyrolyzed saw dust was washed thoroughly with distilled water for 3-4 times until the pH of the solution become constant. After washing, the precipitate was dried in an oven at 100 ^{0}C for 24 hours, cooled it to room temperature and classified with 75 micron mesh to make Activated Sawdust.

To prepare sawdust based chitosan composite beads similar method was used as activated carbon chitosan composite bead preparation. Instead of activated carbon, 0.5 g of sawdust was mixed with chitosan solution and that was added drop wise to 1.0M of NaOH solution.

3.3.4 Preparation of protonated sawdust- chitosan composite beads

After preparing wet sawdust chitosan composite beads, the beads were cross-linked with 2.5 wt. % Glutaraldehyde solution and the ratio of Glutaraldehyde to chitosan bead was approximately 10ml/g of wet beads. Beads were kept in Glutaraldehyde solution for 48 h and then washed with distilled water to remove any free Glutaraldehyde. Then, the cross-linked beads were treated with concentrated HCl for 30 minutes for protonation of beads. Finally, protonated beads were washed with distilled water to a constant pH and dried at room temperature for adsorption studies.

3.4 Characterization of adsorbents using pH of Zero Point Charge (pH_{zpc})

Raw chitosan powder, Activated carbon chitosan composite beads and Protonated sawdust chitosan composite beads were characterized using pH of zero point charge (pH_{zpc}) method.

The pH at which the surface charge of the material is zero in the aqueous media or in other words the pH point of zero charge (pH_{zpc}) of the adsorbent materials was determined using pH drift method.

A series of pH solutions ranging from pH 2 to 12 were prepared by adding hydrochloric acid (HCl) and sodium hydroxide (NaOH) to distilled water. Then, 0.1g of raw chitosan powder, activated carbon chitosan composite beads, and protonated sawdust chitosan composite beads were added to 25 ml of pH solutions. Then, prepared solutions were shaken for 24 hours at 200rpm in 25^0C. The final pH values were recorded after 24 h. The final pH vs. Initial pH graph was plotted and the point of intersection of the resulting curve at 45 degree line gave the pH_{zpc}. HACH sensION+ PH1 portable pH meter was used to measure pH.

3.5 Measuring the Removal Efficiencies of the Adsorbents

Adsorption experiments were carried out for Raw and modified chitosan to study the effects of initial fluoride concentration, contact time and adsorbent dosage on the removal efficiency of fluoride. The fluoride concentration was measured by using a HACH DR 900 multi parameter portable colorimeter. All the experiments were carried out under neutral pH conditions.

The adsorbed amount and the percentage removal of fluoride were calculated by using the following equations,

The adsorption capacity at equilibrium (q_e):

$$\boldsymbol{q_e = \frac{(C_0 - C_e)}{W} V}$$

Where, $\boldsymbol{C_0}$ (mg/l) is initial concentration of adsorbate, $\boldsymbol{C_e}$ (mg/l) is the equilibrium concentration of the adsorbate, W (g) is the weight of the adsorbent added and, V (ml) is volume of solution.

Percentages of removal of fluoride (E %):

$$\boldsymbol{E}(\%) = \frac{(\boldsymbol{C_0} - \boldsymbol{C_e})}{\boldsymbol{C_0}} * \boldsymbol{100}\%$$

Where, E (%) is removal efficiency,$\boldsymbol{C_0}$ (mg/l) is initial concentration and $\boldsymbol{C_e}$ (mg/l) is equilibrium concentration of the adsorbate.

3.5.1 Effect of contact time

The effect of contact time was measured using 25 ml of 5 mg/l fluoride solution at neutral pH in 25^0C. The adsorbent dosage was kept as 2g/l for all raw and modified chitosan. Defluoridation capacity was measured in every 10 minutes interval up to 120 minutes. Fluoride removal (E %) vs. contact time was plotted and the time required to reach the equilibrium was considered as the optimum contact time.

3.5.2 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of fluoride was studied by varying the dosage of adsorbent in the range of 0.5 to 5 g/l. The experiment was carried out in neutral pH in 25^0C. The initial fluoride concentration was 10 mg/l and the experiment was carried out for the optimum contact time value obtained from the previous experiment's results.

3.5.3 Effect of initial fluoride concentration

The Effect of initial fluoride concentration was investigated using varying the fluoride concentrations in the range of 2-10 mg/l. The experiment was carried in neutral pH for optimum contact time in 25^0C. Adsorbent dose of 2g/l was used in this experiment

3.6 Analysis of adsorption isotherm models

To understand the interaction of adsorbate with adsorbent, and to evaluate the maximum adsorption capacities of modified chitosan for the removal of fluoride, two commonly used isotherms namely Langmuir and Freundlich were adopted.

The isotherm study was conducted at pH 7 with a reaction time of 60 minutes and an adsorbent dosage of 2g/L using protonated sawdust chitosan composite beads. Adsorption capacities were calculated varying the initial fluoride concentrations between 2 - 15 mg/L.

3.6.1 Langmuir isotherm model

Langmuir isotherm model can be represent by following sets of equations

$$q_e = \frac{q_m k_a C_e}{1 + k_a C_e}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_a} \frac{1}{C_e}$$

Where q_e(mg/g) is adsorption capacity at equilibrium, C_e (mg/l) is equilibrium concentration of the adsorbate, q_m (mg/g) maximum monolayer sorption capacity, and k_a (L/mg) is the Langmuir isotherm constant.

$$R_L = \frac{1}{1 + k_a C_i}$$

Where C_i is the initial concentration of adsorbate in mg/l. R_L indicates the nature of the adsorption process, as given below:

- $R_L > 1$ Unfavorable
- $R_L = 1$ Linear
- $0 < R_L < 1$ Favorable
- $R_L = 0$ Irreversible

Langmuir equation's constants were determined using the $\frac{1}{q_e}$ vs. $\frac{1}{C_e}$ linear plot .The R_L value was calculated and the nature of the process was identified using that value.

3.6.2 Freundlich model

Freundlich isotherm model can be represent by following sets of equations

$$q_e = k_f C_e^{1/n}$$

$$log q_e = log k_f + \frac{log C_e}{n}$$

Where q_e (mg/g) is adsorption capacity at equilibrium, C_e (mg/l) is equilibrium concentration of the adsorbate, k_f (mg/g) Freundlich isotherm constant (mg/g) related to adsorption capacity and n is the adsorption intensity n indicates the nature of the adsorption process, as given below (Aljeboree, et al., 2014)

- $n = 1$ adsorption is linear
- $n < 1$ adsorption process is chemical
- $1 < n < 10$ adsorption is a favorable physical process

Freundlich equation's constants was determined using log q_e vs log C_e linear plot. The n value was calculated and the nature of the process was identified using that value.

The results were plotted in Langmuir isotherm model and Freundlich isotherm model and the best fitted isotherm model was identified using correlation coefficient (R^2). Using that model, maximum adsorption capacity of the adsorbent was calculated.

3.7 Analysis of adsorption kinetic models

To investigate the adsorption mechanism and rate of modified chitosan, pseudo-first order and pseudo-second-order kinetic models were used.

Adsorption kinetics studies for protonated sawdust chitosan composite beads were conducted on the fluoride removal using a synthetic fluoride solution with concentration of 5 mg/l by maintaining the pH at 7 and adsorbent dosage of 2g/L. Samples were collected at appropriate time intervals and the adsorption capacities were calculated. The obtained results were modeled using Pseudo first order model and Pseudo second order model.

3.7.1 Pseudo first order model

Pseudo first order model can be represent by following sets of equations

$$\mathrm{q}_t = q_e(1 - e^{-k_1 t})$$

$$\ln(q_e - q_t) = lnq_e - k_1 t$$

Where q_e (mg/g) is adsorption capacity at equilibrium, q_t (mg/g) is adsorption capacities at time t, k_1 (1/min) is the rate constant of pseudo-first-order adsorption.

Pseudo first order equation's constants were determined using $\ln(q_e - q_t)$ vs. t linear plot.

3.7.2 Pseudo second order model

Pseudo second order model can be represent by following sets of equations

$$\mathrm{q}_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

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

Where q_e (mg/g) is adsorption capacity at equilibrium, q_t (mg/g) is adsorption capacities at time t, k_2 (g/mg/min) is the rate constant of pseudo-second-order adsorption.

Pseudo second order equation's constants were determined using $\frac{t}{q_t}$ vs t linear plot.

The correlation coefficient (R^2) was be employed as error analysis method to determine the best-fitting equations for kinetic models. (Lin, et al., 2009)

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Preliminary work

4.1.1 Characterization of ACCCB using pH of Zero Point charge (pH_{zpc})

The pH of zero point charge describes the pH where the electrical charge of a particle's surface is zero. The surface of the particle is negatively charged at pH values larger than the pH_{zpc} and positively charged at pH values lower than the pH_{zpc}.

Figure 4.1 shows the pH_{zpc} of Activated Carbon Chitosan Composite Beads (ACCCB). According to the experimental results pH_{zpc} of ACCCB is 7.0. The obtained results suggest that there is no surface charge of the beads when conducting the experiments in pH 7. Hence, the removal is only possible owing to the physisorption process.

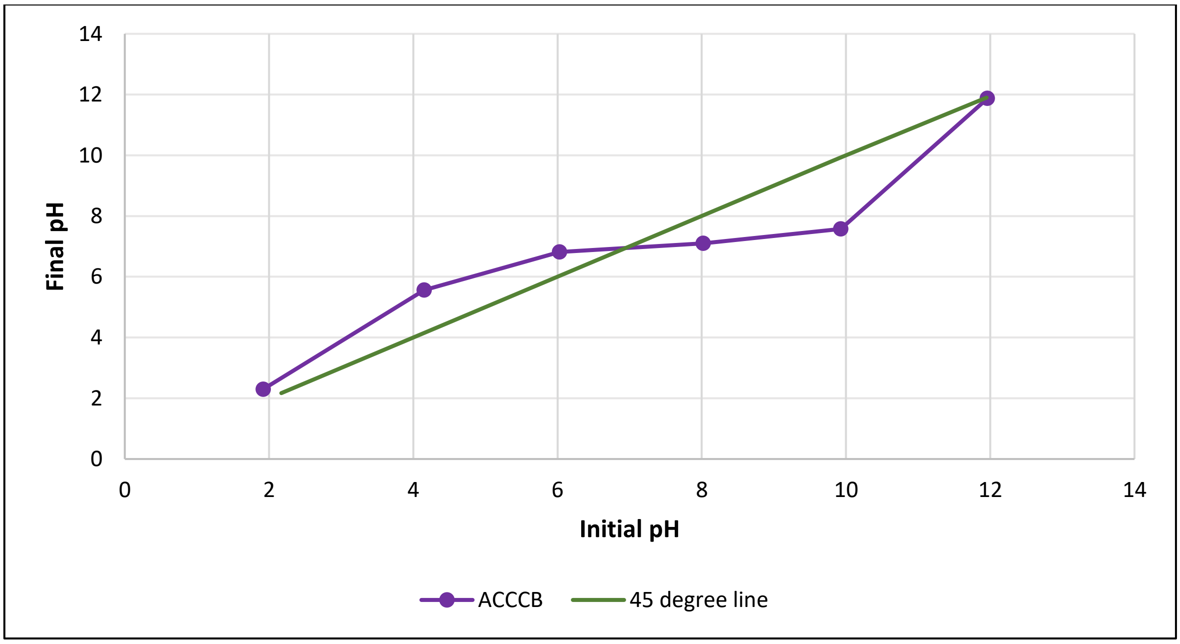

Figure 4.1 pH of zero point charge of ACCCB (Temperature = 25^0C; Contact time = 24 hours; Adsorbent dosage = 4g/l)

4.1.2 Effect of adsorbent dosage

Figure 4.2 illustrates the effect of adsorbent dosage on fluoride removal efficiencies and adsorption capacities of ACCCB. All the experiments were conducted at 25^0C, at pH 7 with a reaction time of 2 hours using 25ml of standard fluoride solutions for 1, 2 and 3 g/L dosages. The initial fluoride concentration was 10 mg/l.

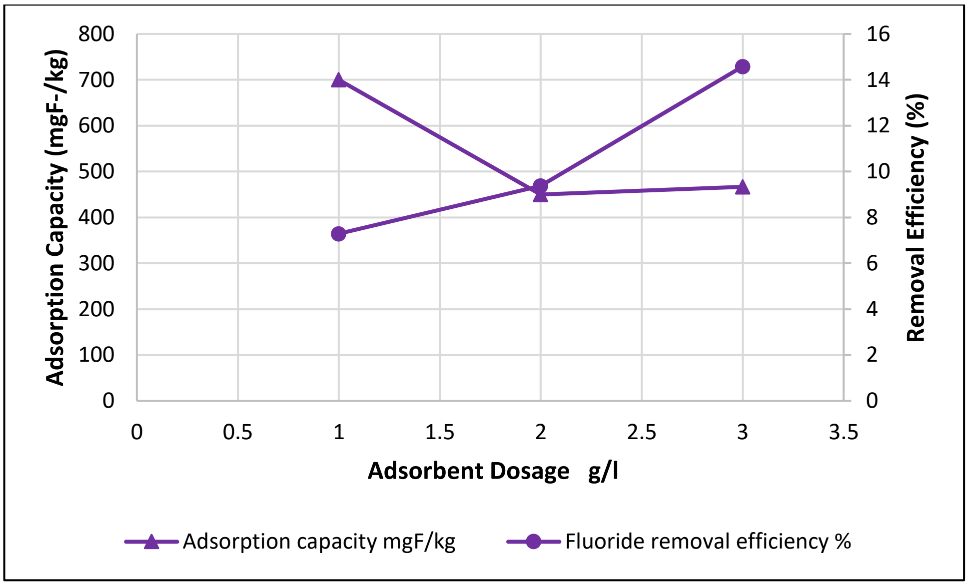

Figure 4.2 Adsorption of fluoride as a function of adsorbent dosage for ACCCB (Temperature = 25^0C; Contact time = 120 min; Initial fluoride concentration = 10 mg/l; pH = 7)

The adsorption capacity of ACCCB decreased when increased the adsorbent dosage. This may be due to the availability of too many active sites for limited amount of fluorides (Xu, et al., 2011). The removal efficiencies increased when increased the adsorbent dosage due to number of active sites increases with increasing dosage, hence the increase in removal efficiency. Therefore the highest removal efficiency was achieved by 3g/l of the adsorbent.

4.1.3 Effect of initial fluoride concentration

The effect of initial fluoride concentrations on defluorodization capacity was studied at pH 7 and 25^{0}C. Figure 4.3 shows the influence on varying the initial fluoride concentration on the fluoride removal by the adsorbent. It was found that removal efficiency is increasing with high initial concentrations. This may be due to higher concentration act as a driving force to overcome mass transfer resistance between bulk solution and adsorbent surface (Banerjee, et al., 2013).

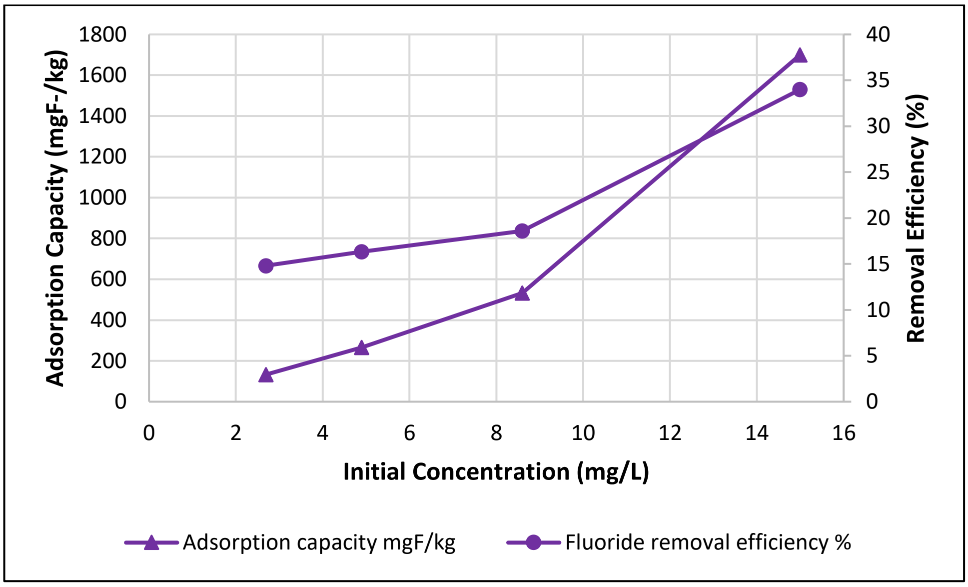

Figure 4.3 Adsorption of fluoride as a function of initial fluoride concentration for ACCCB (Temperature = 25^{0}C; Contact time = 120 min; Adsorbent dosage = 3g/l; pH = 7)

4.1.4 Effect of contact time

Figure 4.4 illustrates the fluoride removal efficiencies of ACCCB in 30, 60, 90, and 120 minutes using 25ml of standard fluoride solution at pH 7 with concentration of 5mg/l and an adsorbent dose of 3g/l.

It is observed that at the beginning fluoride adsorption occurred rapidly (within first 60 minutes) and thereafter proceed at a lower rate and finally reach the equilibrium at 120 minutes. The rapid adsorption within first 60 minutes may be due to the adsorption on the outer surface and thereafter adsorption took place slowly inside the pores (Geethamani, et al., 2014). It was found that the ACCCB possesses a maximum adsorption capacity of 233 mg F^-/kg and a maximum removal efficiency of 15%.

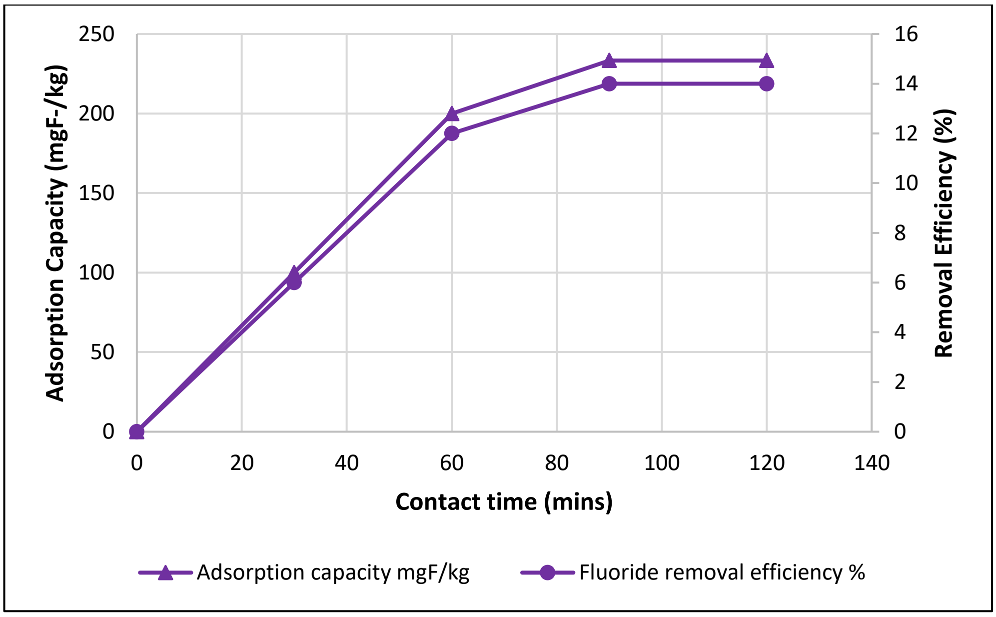

Figure 4.4 Adsorption of fluoride as a function of contact time for ACCCB (Temperature = 25^0C; Initial fluoride concentration = 5 mg/L; Adsorbent dosage = 3g/l; pH = 7)

4.1.5 Fluoride removal efficiency of ACCCB, SCCB and PSCCB

Since Activated Carbon Chitosan Composite Beads (ACCCB) couldn't perform to the required removal Sawdust Chitosan Composite Beads (SCCB) was prepared. Under the same conditions, maximum removal of SCCB was found to be 22% whereas ACCB only showed 15% of fluoride removal. Similarly, SCCB performance is not adequate to remove fluoride efficiently. Thus, Sawdust chitosan composite beads were chemically modified to prepare Protonated Sawdust Chitosan Composite Beads (PSCCB). The removal efficiency of PSCCB was found to be 85% for the above conditions. Fluoride removal efficiencies of modified adsorbent materials are shown in Figure 4.5. Therefore, Protonated Sawdust Chitosan Composite Beads (PSCCB) were used as the final modified adsorbent in subsequent studies.

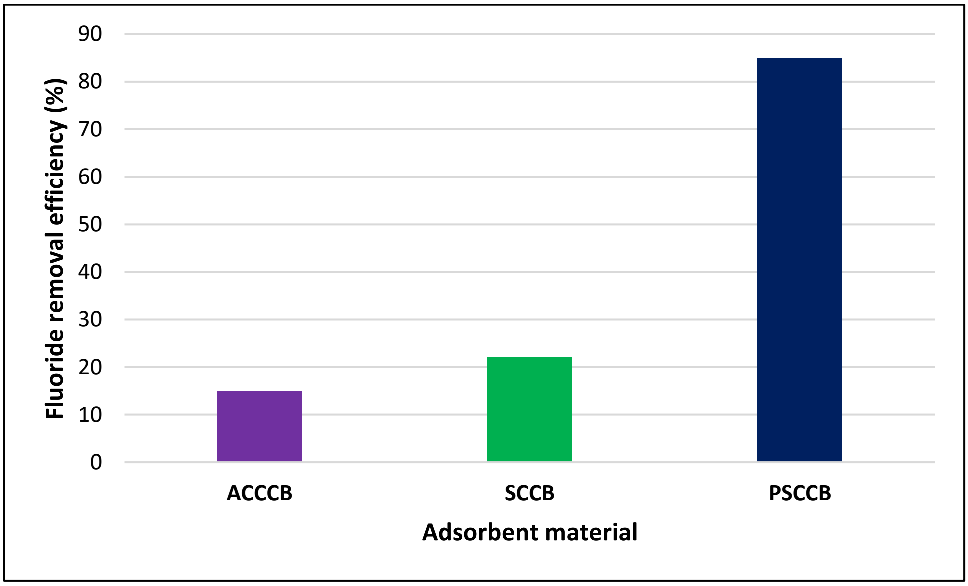

Figure 4.5 Fluoride removal efficiencies of modified adsorbent materials (Temperature = 25^0C; Initial fluoride concentration = 5 mg/L; Adsorbent dosage = 3g/l; pH = 7; Contact time = 120 minutes)

4.2 Characterization of the Adsorbents

In this study raw chitosan powder was considered as the raw adsorbent and Protonated Sawdust Chitosan Composite Beads (PSCCB) were considered as the modified adsorbent.

4.2.1 pH of Zero Point Charge (pH_{zpc})

pH of zero point charge indicates the pH at which the surface electrical charge of an adsorbent is zero. At pH values larger than pH_{zpc} the surface charge of the adsorbent gets negative while at pH values lower than pH_{zpc}, the surface charge of the adsorbent gets positive. Since the batch experiments were conducted at neutral pH and with fluoride being a negative ion, the ability of the adsorbent material to remove fluoride could be well understood by determining zero point charge of the adsorbent.

The pH_{zpc} studies were conducted for both raw and modified chitosan (PSCCB) and the results obtained are depicted in figure 4.6. Experimental results indicate that the pH_{zpc} of raw chitosan is 7 and in the modified adsorbent pH_{zpc} is 2.2.

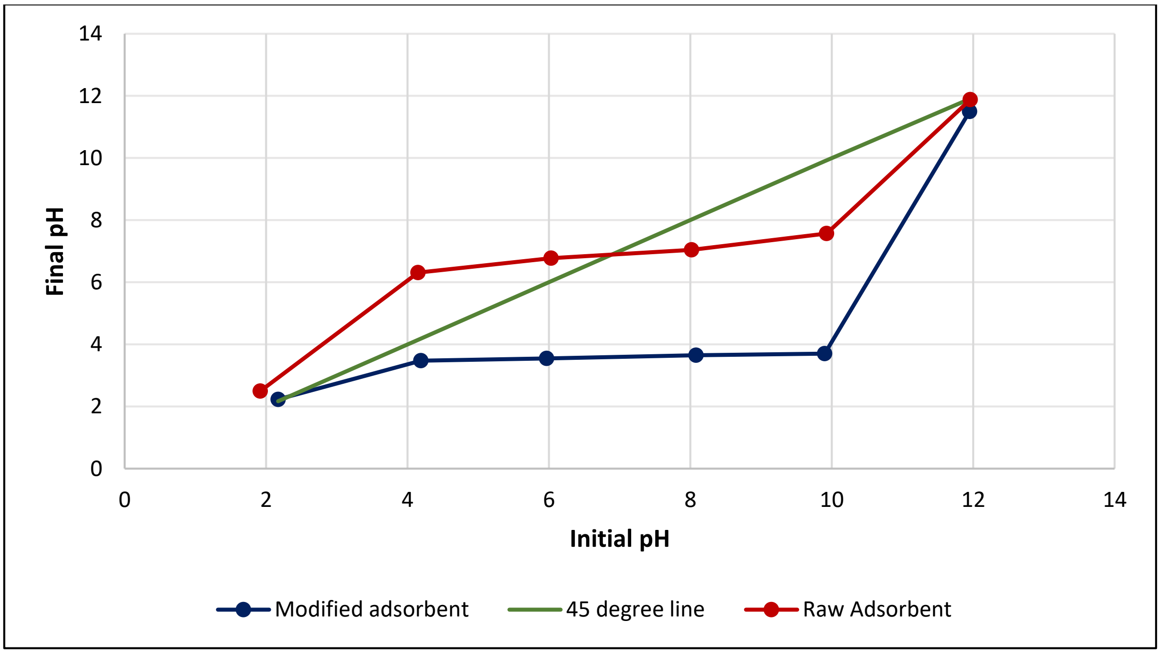

Figure 4.6 pH of zero point charge of Raw and Modified adsorbent (Temperature = 25^0C; Contact time = 24 hours; Adsorbent dosage = 4g/l; pH = 7)

According to the results obtained, there was no surface charge in the raw chitosan at neutral pH, hence it suggest that the raw chitosan cannot be effectively used in removing negatively charged fluoride at neutral pH. However, with pH_{zpc} being 2.20 for modified chitosan its surface gets negatively charged at neutral pH, hence it indicates that the material has undergone some kind of modification.

4.3 Adsorption Studies.

In this adsorption studies raw chitosan powder was considered as the raw adsorbent and Protonated Sawdust Chitosan Composite Beads (PSCCB) were considered as the modified adsorbent.

4.3.1 Effect of Contact Time.

Figure 4.7 shows the results of the contact time test carried out for both raw and modified chitosan for initial fluoride concentration of 5 mg/L. A rapid fluoride adsorption was observed initially and thereafter gradually reaching the equilibrium. The rapid uptake observed may be due to the adsorption on the outer surface, and thereafter, adsorption took place slowly inside the pores (Geethamani, et al., 2014). As time elapses as the fluoride concentration in the solution gets reduced thus reducing the concentration gradient between the bulk solution and the adsorbent surface and thereby reducing the net driving force to overcome the resistance between bulk solution and adsorbent surface (Anbia, and Salehi 2012). In addition to this the active sites available for adsorption also get reduced with the uptake of fluoride and thus, these facts could explain the adsorption behavior resulted from contact time test for both raw and modified chitosan.

It is interesting to note that the equilibrium time of modified chitosan was around 60 minutes while raw chitosan reached equilibrium at around 120 minutes as reflected in Figure 4.7. Excellent removal efficiency was recorded for modified chitosan which was more than 90% at equilibrium, whereas only 16% of maximum removal efficiency was observed for raw chitosan at the time of equilibrium and it is also depicted in Figure 4.7. Moreover, since chitosan has been modified both physically and chemically a mixed mechanism of adsorption is observed in the modified chitosan unlike the raw chitosan. This explains the desorption that happens from time to time with modified chitosan.

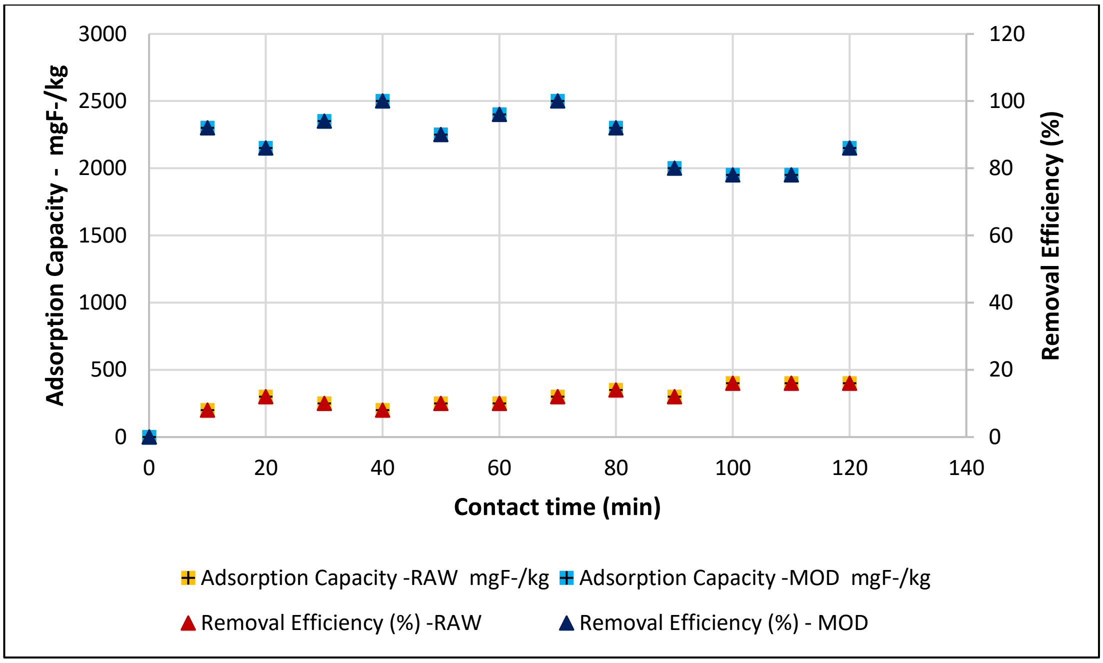

Figure 4.7 Adsorption of fluoride as a function of contact time (Temperature = 25^0C; Initial fluoride concentration = 5 mg/L; Adsorbent dosage = 2g/l; pH = 7)

4.3.2 Effect of Adsorbent Dosage

The effect of adsorbent dosage was investigated for both raw and modified chitosan and the results are illustrated in Figure 4.8. The fluoride adsorption capacity of both raw and modified chitosan decreased with an increase in adsorbent dosage while fluoride removal efficiency increased in modified adsorbent. The increase in removal efficiency can be attributed to the availability of active sites and increased surface area when dosage increases from 0.5 g/L to 5 g/L, whereas the decrease in adsorption capacity is due to presence of unsaturated sites during the adsorption process as the initial fluoride concentration is kept constant (Anbia, and Salehi, 2011). Similar observations were made by Meenakshi et al (2008) in their study on fluoride removal.

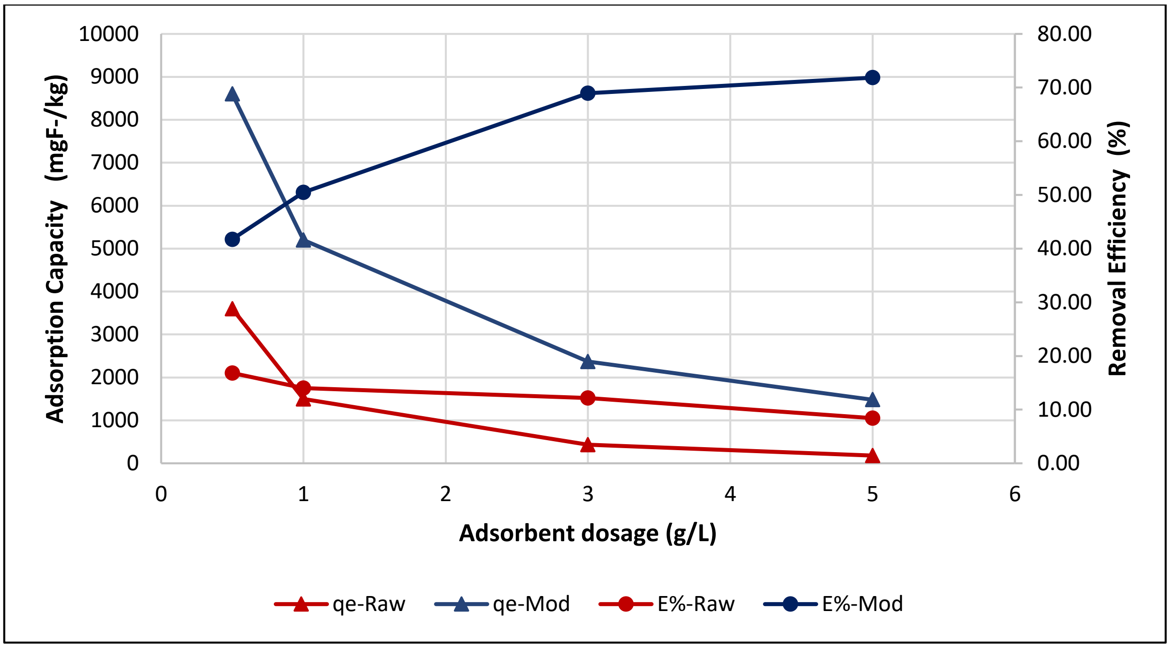

Figure 4.8 Adsorption of fluoride as a function of adsorbent dosage (Temperature = 25^0C; Contact time = 60 min for Mod. Adsorbent and 120 min for Raw adsorbent; Initial fluoride concentration = 10 mg/l; pH = 7)

4.3.3 Effect of initial fluoride concentration

The adsorption of fluoride onto raw and modified chitosan was carried out for initial concentrations ranging from 2 mg/L to 15 mg/L while keeping other parameters constant and the result obtained are illustrated in Figure 4.9. It was observed that the adsorption capacity of both raw and modified chitosan increased when initial fluoride concentration increased. The reason behind this observation is that at higher fluoride concentrations there is high concentration gradient acting as a driving force to overcome mass transfer resistance between bulk solution and adsorbent surface. The decrease in fluoride removal efficiency was observed in both cases since there is limited number of adsorption sites to accommodate fluoride ions for a certain amount of adsorbent dosage (Patnaik et al., 2016). As for raw chitosan the adsorption capacity decreased with increase in initial fluoride concentration. This could be a result of fluoride ions not being able to come in contact with active sites of the adsorbent.

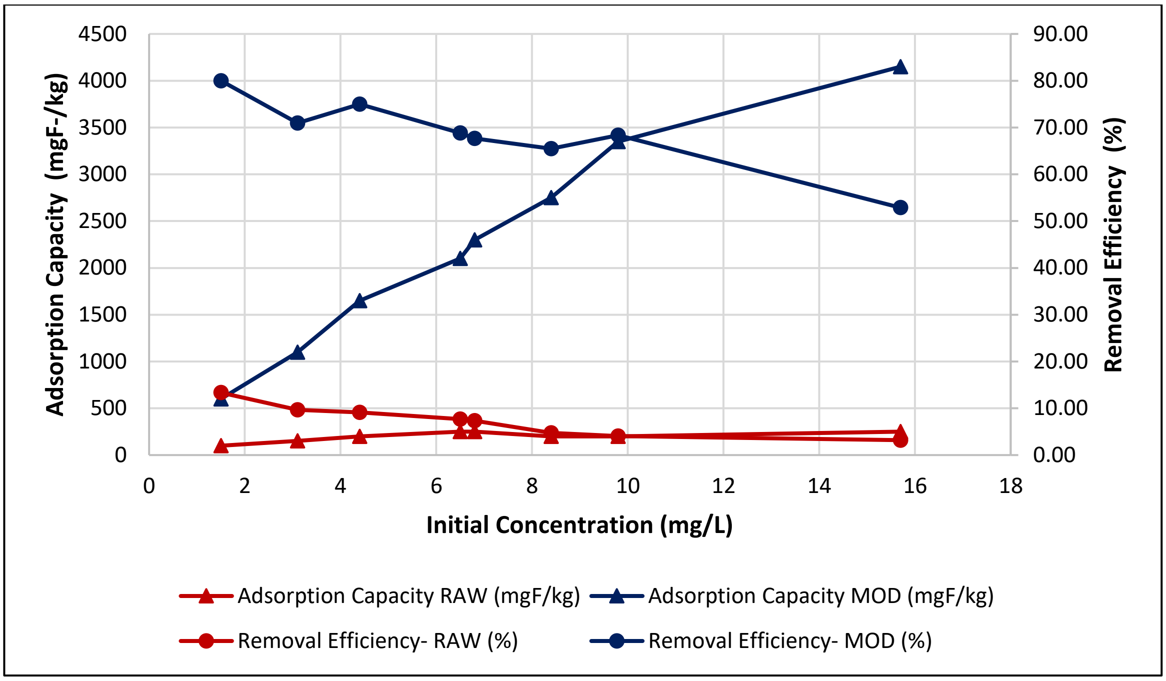

Figure 4.9 Adsorption of fluoride as a function of initial fluoride concentration (Temperature = 25^{0}C; Contact time = 60 min for Mod. Adsorbent and 120 min for Raw adsorbent; Adsorbent dosage = 2g/l; pH = 7)

4.4 Sorption Isotherm studies

Isotherm Studies were done only for the modified adsorbent as it showed higher removal capacity than the raw adsorbent.

In order to quantify the adsorption capacity of modified chitosan for the removal of fluoride, and to identify how adsorbate interacts with adsorbents Langmuir and Freundlich isotherms were used to model adsorption equilibrium data. The experimental data of the equilibrium studies are depicted in Figure 4.10.

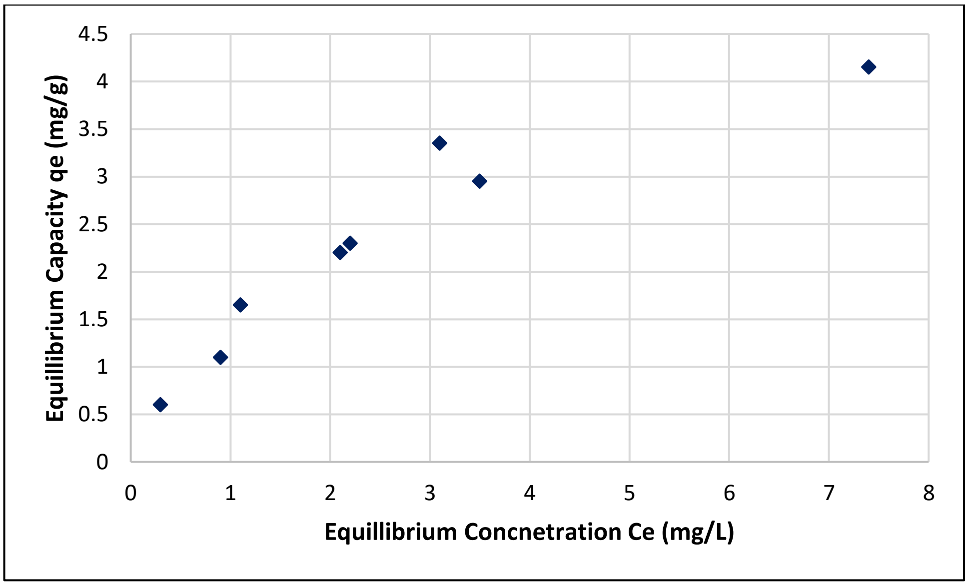

Figure 4.10 Adsorption isotherm studies for fluoride adsorption (Temperature = 25^{0}C; pH = 7; contact time = 60 min; Adsorbent dosage= 2 g/l)

The Langmuir isotherm is based on the assumption that adsorption process is monolayer and adsorption occurs at homogeneous sites with equal affinity towards adsorbate. The Freundlich isotherm assumes that the adsorption process takes place on heterogeneous surfaces by multilayer adsorption where binding sites have varying affinity towards adsorbate. The analysis of experimental data using Langmuir and Freundlich isotherm models are presented in Figure 4.11 and Figure 4.12 respectively.

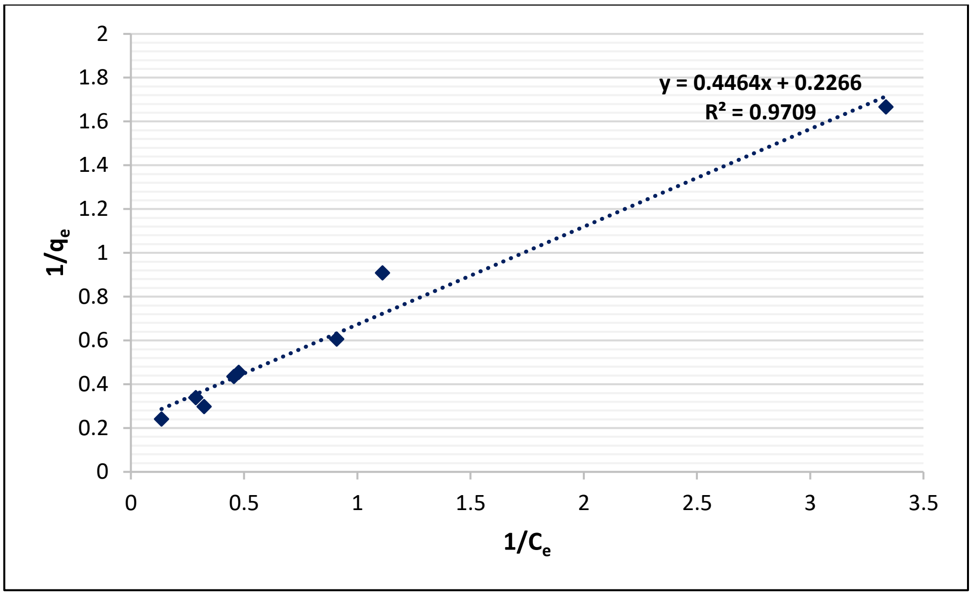

Figure 4.11 Determination of Langmuir equation’s constants

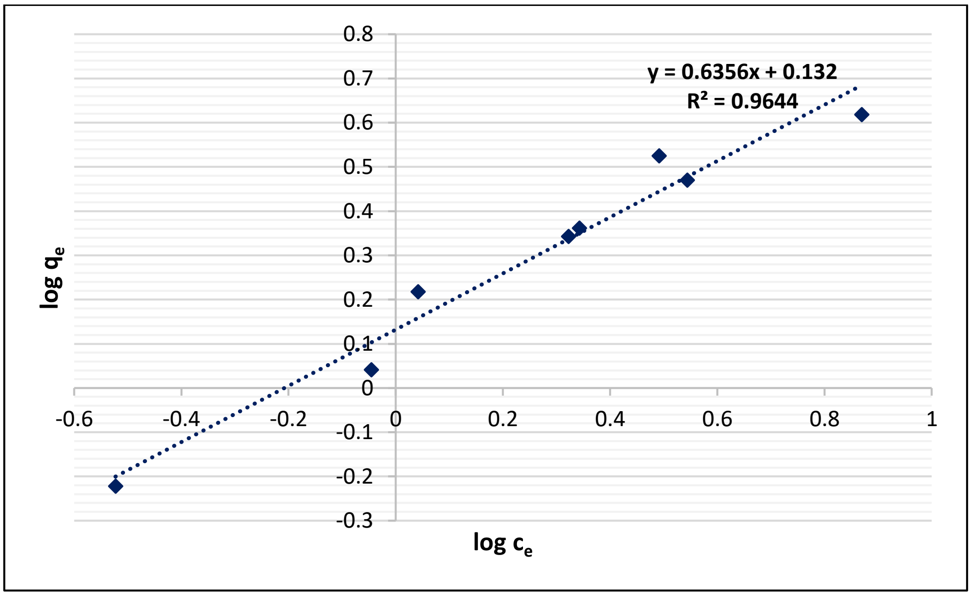

Figure 4.12 Determination of Freundlich equation’s constants.

According to the linear form of Langmuir equation $(\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_a}\frac{1}{C_e})$ plot of $1/q_e$ against $1/c_e$ yields a straight line and constraints obtained from slope and intercept of the linear regression plot of experimental data are summarized in Table 5.1.

According to the linear form of Freundlich equation ($log q_e = log k_f + \frac{log C_e}{n}$) plot of log q_e against log c_e yields a straight line and constraints obtained from slope and intercept of the linear regression plot of experimental data are summarized in Table 4.1.

Table 4.1 Parameters of isotherm equations

Isotherm	**Parameters**	**R^2**
Langmuir	q_m = 4.413 mg/g	0.9709
	k_a = 0.5076 L/mg	
	R_L = 0.2826	
Freundlich	k_f = 1.355 mg/g	0.9644
	n = 1.573	

From the results tabulated in Table 4.1 the highest correlation coefficient is recorded for Langmuir isotherm which indicates the applicability of Langmuir isotherm model with the experimental data of modified chitosan. According to Langmuir isotherm the maximum monolayer adsorption capacity is 4413 mgF^-/kg. R_L is between 0 and 1 which indicates the nature of the adsorption process is favorable.

4.5 Sorption Kinetic Studies

Kinetic Studies were done only for the modified adsorbent as it showed higher removal capacity than the raw adsorbent.

In order to further understand the characteristics of fluoride uptake on to modified chitosan, two of the reaction based kinetic models were applied on to the contact time data conducted for 60 min with initial fluoride concentration of 5 mg/L at neutral pH. Two of the most commonly used Pseudo first order model and pseudo second order model were employed to the kinetic analysis of fluoride adsorption onto modified chitosan. It could be observed from Figure.4.13 that at the beginning there is rapid uptake of fluoride and thereafter gradually reaching the equilibrium. A sudden uptake of fluoride in the first 10 min period emphasizes that adsorption could be much critical during that period.

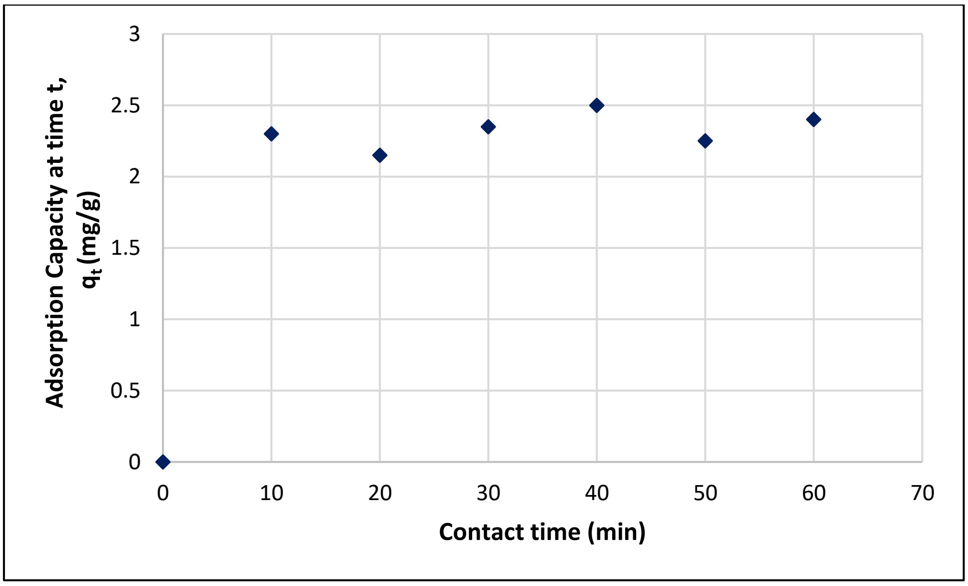

Figure 4.13 Adsorption kinetic studies for fluoride adsorption (Temperature = 25^0C; Initial fluoride concentration = 5 mg/l; Adsorbent dosage = 2g/l; pH = 7)

The plot of pseudo first order model is depicted in Figure 4.14. From the equation ($\ln(q_e - q_t) = lnq_e - k_1 t$) linear plot of log ($q_e$-$q_t$) against t gives a straight line. The values of correlation coefficient and K_1 is computed from this plot through linear regression and results are tabulated in Table 4.2 (q_t is the amount of fluoride on the surface of the sorbent at time t and K_1 is the equilibrium rate constant of pseudo first order adsorption).

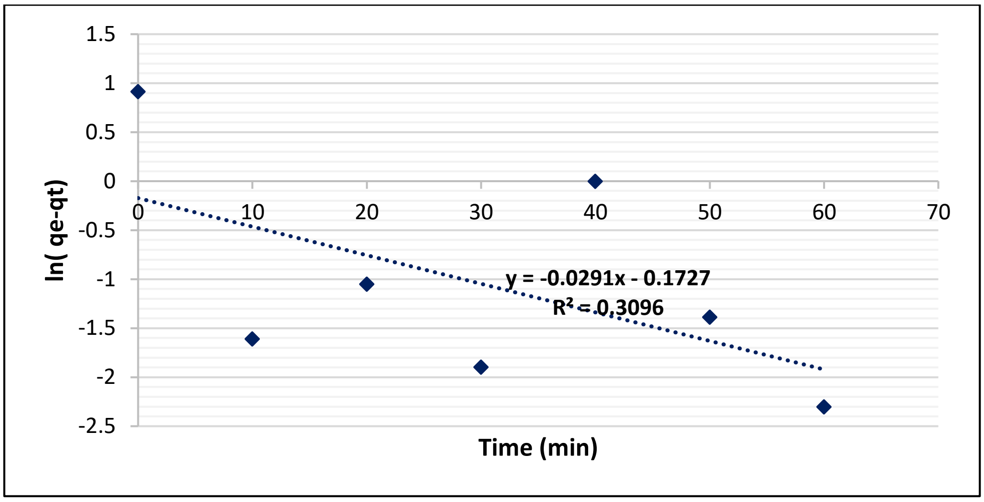

Figure 4.14 Determination of Pseudo first order equation’s constants

The plot of pseudo second order model is depicted in Figure 4.15. From the equation ($\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$) linear plot of t/$q_t$ against t gives a straight line. The values of correlation coefficient and k_2 is computed from this plot through linear regression and results are tabulated in Table5.2. (t is the contact time between adsorbate and adsorbent (min), qt and qe are the contents of adsorbate removed by adsorbent at an arbitrary time t and at equilibrium (mg/g), respectively, and k is the rate constant (g/mg min).

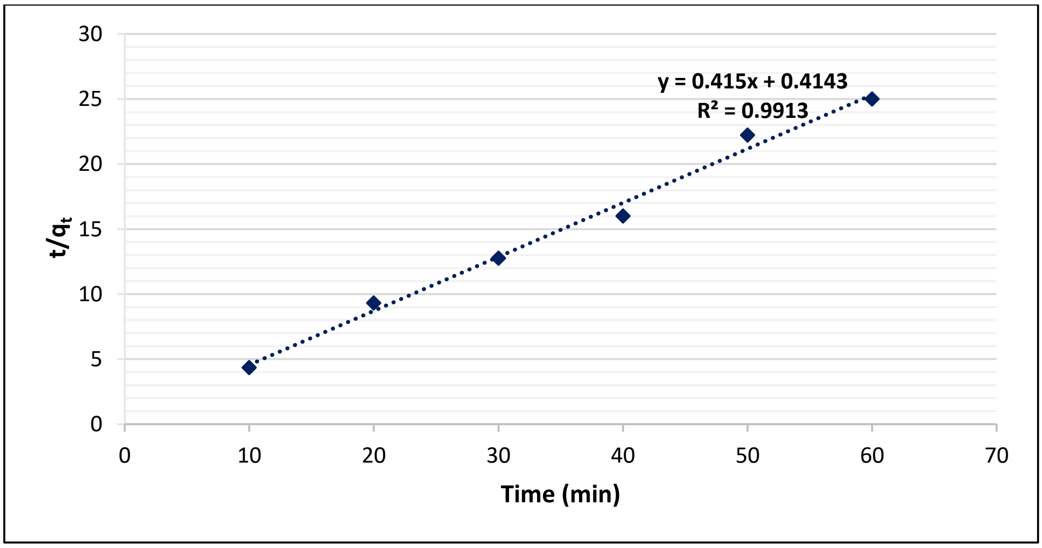

Figure 4.15 Determination of Pseudo second order equation’s constants

Table 4.2 Kinetics coefficient values (Reaction models)

Kinetic Model	**Parameter**	**R^2**
Pseudo first order	q_e = 1.488 mg/g	0.3096
	k_1 = 0.0291 l/min	
Pseudo second order	q_e = 2.409 mg/g	0.9913
	k_2 = 0.4157 g/mg/min	

The results tabulated in Table 4.2 indicates the applicability of pseudo second order model than pseudo first order model when correlation factors are observed. This suggests that the adsorption process is controlled by chemisorption (Xu, et al., 2011). According to Pseudo second order model adsorption capacity at equilibrium is 2409 mgF$^-$/kg and the rate constant of pseudo second order adsorption is 0.4157 g/mg/min. Even though studies for fluoride adsorption for initial concentrations below 10 mg/L are very limited Vishwanathan et al., 2009 have conducted a similar study using multifunctional chitosan beads and obtained equilibrium removal capacity of 2.2 mg/g where it fits into pseudo second order model at initial concentration of 11 mg/L and observed to have an decreasing trend in removal capacity with decreasing initial fluoride concentration. When compared with this result, for protonated chitosan-saw dust composite beads, with having an adsorption capacity of 2.409 mg/g at equilibrium, for initial concentration of 5 mg/L, it has improved to a greater extent. Meenakshi et al., 2008 obtained 1.871 mg/g of adsorption capacity for their protonated chitosan beads according to pseudo second order model for an initial concentration of 11 mg/L of fluoride and this again confirms that the protonated sawdust chitosan composite beads (PSCCB) possess higher adsorption capacity even at very low initial fluoride concentration levels.

CHAPTER FIVE

CONCLUSIONS AND RECOMMONDATIONS

5.1 Conclusions

Chitosan is an effective biosorbents which could be used to effectively remove fluoride when prepared in bead form. Raw chitosan powder showed a very low fluoride removal efficiency, as low as 16% at equilibrium. This observation could be supported by the characterization made in the zero-point charge test where it was found that surface of raw chitosan is charged neutral at pH 7, where its pH_{zpc} was also at pH 7. The experiments were conducted at pH 7 owing to the fact that groundwater is at neutral pH.

In the process of modifying chitosan, initially, Activated Carbon Composite Beads (ACCB) were prepared but could not perform up to the required level of fluoride removal. ACCB was found to have only 15% of fluoride removal at equilibrium. Since pH_{zpc} was at pH 7 for ACCB and therefore, being surface neutral at neutral pH could have been the reason behind above observation.

Another modification was carried out by preparing Sawdust Chitosan Composite Beads (SCCB) to increase the fluoride removal capacity. Even though a higher fluoride uptake of 22% could be reached using SCCB, it was not enough to bring down the fluoride level below 1 mg/L as required. Since physically modifying the chitosan alone could not bring better results, chitosan was then chemically modified by crosslinking followed by protonation to induce adsorption via chemical bonding to further enhance the adsorption capacity of chitosan to form Protonated Sawdust Chitosan Composite Beads (PSCCB).

Protonated Sawdust Chitosan Composite beads were found to have an excellent defluoridation capacity compared to raw chitosan. The effect of various influencing parameters such as contact time, adsorbent dosage and initial fluoride concentration on synthetic fluoride solutions were investigated via batch experiments. All the experiments were conducted at neutral pH since groundwater is considered to be at neutral pH.

More than 90% removal efficiency was observed for an equilibrium time of 60 minutes for PSCCB. The zero-point charge of PSCCB was found to be 2.2 and it suggests the occurrence of structural changes on the surface of the adsorbent. Since all the experiments are carried out at pH 7 and for $pH_{zpc} < pH\ 7$: the surface charge of the adsorbent is negative and the higher adsorption capacity at neutral pH could be attributed to availability of surface complexities rather than electrostatic attraction.

Equilibrium study shows that for PSCCB, the data fit well with Langmuir isotherm with a high R^2 value of 0.9709 indicating the sorption process is monolayer and nature of adsorption is chemical. The maximum adsorption capacity according to Langmuir isotherm was found to be 4413 mgF^-/kg. The kinetics of PSCCB followed pseudo second order with an assumption that the rate limiting step is a chemisorption which again confirms that the adsorption happens via chemical bonding. A higher R^2 value of 0.9913 was recorded for pseudo second order model through linear regression, compared to pseudo first order model. Considering all the above facts, it could be said that Protonated Saw dust Chitosan Composite beads can be used effectively for removal of fluoride from water.

5.2 Recommendations

In order to get a better understanding of the mechanism of adsorption and availability of functional groups of Protonated Chitosan Saw dust composite beads, the characterization using SEM, FTIR, BET and Particle size analysis must be carried out.

An attempt must be made to investigate the applicability of Protonated Chitosan Saw dust composite beads on actual groundwater samples for the completion of the study.

Further studies must be carried out to understand how protonation followed by crosslinking has affected the activated sawdust in the composite beads.

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