

**AN INVESTIGATION INTO THE REMOVAL OF FLUORIDE
FROM DRINKING WATER BY ADSORPTION**



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2010-NUST-MSPHD-Env S-07

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Islamabad, Pakistan

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By

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(2010-NUST-MSPHD-Env S-07)

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It is certified that the contents and form of the thesis entitled

**“AN INVESTIGATION INTO THE REMOVAL OF FLUORIDE
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LIST OF ABBREVIATIONS

Abbreviation	Description
AA	Activated Alumina
AC	Activated Charcoal
APHA	American Public Health Association
MIAA	Modified Immobilized Activated Alumina
NSDWQ	National Standards for Drinking Water Quality
UNEP	United Nations Environment Program
WHO	World Health Organization
WWF	World Wide Fund for Nature
WQA	Water Quality Association

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ABSTRACT

The study describes the removal of fluoride from drinking water using modified immobilized activated alumina (MIAA) prepared by sol-gel method. The modification was done by adding specific amount of alum during the sol formation step. The fluoride removal efficiency of MIAA was 1.35 times higher as compared to normal immobilized activated alumina.

Batch adsorption study was performed as a function of adsorbent dose, contact time, stirring rate and initial fluoride concentration. More than 90% removal of fluoride was achieved within 60 minutes of contact time. The maximum adsorption capacity was 0.76mg/g at initial fluoride concentration of 12 mg/L and adsorbent dose of 10g/L, within the contact time of 60 minutes and stirring rate of 150rpm at $20\pm 1^{\circ}\text{C}$. The adsorption potential of MIAA was compared with activated charcoal and activated alumina which showed that removal efficiency was about 10% more than activated charcoal and 5% more than activated alumina. Both the Langmuir and Freundlich adsorption isotherms fitted well for the fluoride adsorption on MIAA with the regression coefficient R^2 of 0.99 and 0.98, on AC with R^2 of 0.99 and 0.97, on AA 0.98 and 0.98 respectively.

MIAA can both be regenerated thermally and chemically. Adsorption experiments using MIAA were employed on real drinking water samples from fluoride affected area. The study showed that modified immobilized activated alumina is an effective adsorbent for fluoride removal.

INTRODUCTION

Water is an essential commodity for sustaining life and environment that have always thought to be an inexhaustible resource. In the new era, the Earth, with its diverse and abundant life forms, including over eight billion humans, is facing a serious water crisis. In the perspective of water crises, pollution is one of the major dilemma that has worsens the ecosystem and health situation of people over the past few decades (WWF, 2007). Many pollutants from industrial and agricultural wastewater contaminate the lakes, rivers and ground water aquifers. In drinking water most of the pollutants do not have any color or odor thus even clear water may not be safe. According to World Health Organization (WHO), fluoride is classified as one of the water contaminant which causes health problems (WHO, 2006).

Fluoride has beneficial as well as harmful effects on the human health depending upon its level. The advantageous effect of fluoride in human body is strengthening of bones and preventing tooth decay. According to National Standards for Drinking Water Quality (2010) of Pakistan and WHO (2006) the permissible limit of fluoride in drinking water is 1.5mg/L. Above this limit fluoride can lead to various diseases such as skeletal and dental fluorosis, cancer, brain damage, infertility, Alzheimer disease and thyroid disorder (Ahmed *et al.*, 2003).

Wastewater from many industries contains high level of fluoride. The industries include coal fired power plants, fertilizer industry, glass and semiconductor

manufacturing and rubber manufacturing. So there is a need to remove the excess fluoride from water effectively (Li *et al.*, 2001).

Technologies available for defluoridation include coagulation and precipitation (Gumbo and Mkongo, 1995; Dahiet *al.*, 1996) membrane process (Sehn, 2008), ion exchange (Singh *et al.*, 1999) and adsorption process (Ali and Gupta, 2007). Although coagulation-precipitation which is known as Nalgonda technique is effective and cheap method but the main disadvantage is the generation of chemicals and waste disposal issues. The membrane and ion process is mainly the reverse osmosis technique but it requires maintenance cost due to fouling and scaling of membrane. Similarly the ion exchange process is very costly (Ayoobet *al.*, 2008). The adsorption method is considered more suitable for defluoridation because process is simple, effective and economically viable (Ayoob and Gupta, 2009)

There are many adsorbents used for fluoride removal such as activated alumina (Tang *et al.*, 2009), activated charcoal (Emmanuel *et al.*, 2008), zeolite (Onyangoet *al.*, 2006), many biosorbents (Kambleet *al.*, 2007) and nano sorbents (Li *et al.*, 2001). In recent years there is a growing movement towards the use of natural materials like clay, ash, bone charcoal in developing countries as these materials make the defluoridation method very economical and cheap. However, these economical adsorbents have not displayed significant fluoride removal capacities and, thus, alumina still remains a most effective adsorbent (Stewart, 2009). But it has some limitations in regeneration capacity and poor structure. Many studies have been conducted to improve its efficiency (Lucy *et al.*, 2010).

The main challenge encountered during adsorption studies is the separation of adsorbent from water samples. Generally, filtration is employed for the separation of powdered adsorbent from the water samples. The aim of the present study was to prepare an immobilized adsorbent in the form of beads that could easily be removed from water without undergoing filtration and centrifugation processes. For this purpose, sol gel method has been adopted to prepare immobilized activated alumina with high and uniform surface properties (Buelna and Lin, 1999). The objectives of the present study were

- Synthesis and modification of immobilized activated alumina.
- Comparison of Modified Immobilized Activated Alumina (MIAA) with powdered activated charcoal and powdered activated alumina.
- Application of MIAA on real water samples containing fluoride.

LITERATURE REVIEW

2.1 Background

Fluoride naturally present in environment. Fluoride has beneficial and harmful impacts on human health detrimental to its level in human body and environment and duration of exposure. There is a narrow beneficial concentration range of fluoride with respect to human health. Fluoride prevents tooth decay if the fluoride level is 1 mg/L in drinking water. Above 1.5mg/L fluoride can cause dental fluorosis and in extreme cases skeletal fluorosis.

There are about 40 countries that are affected by fluorosis. The reason for high fluoride level is either natural occurrence in ground water or industrial wastewater. High fluoride concentration is a problem in developing countries mainly because of lack of suitable infrastructure and effective methodologies for treatment (Feenstraet *al.*, 2007).

2.2 Fluoride in Environment

Fluorine is a halogen and powerful electronegative agent. It is a flammable gas. Because of its high reactivity it does not found in its elemental form and exists as fluorides. Fluoride makes approximately 0.08% of earth crust. The most common fluoride containing compounds are fluorspar, cryolite, and fluorapatite (WQA, 2004)

Fluoride naturally present in all water. The fluoride level in sea water is approximately 1 mg/L; river and lakes contain about 0.5 mg/L but in ground water varies. The major source of fluoride in ground water is fluoride containing rocks weathering. Various rocks like granite, basalt, shale and syenite contain fluoride. Fluoride is also present in minerals like topaz, fluorite, fluorapatite, cryolite, phosphorite, theorapatite, etc (Singh and Maheshwari, 2001; Bhatnagaret *al.*, 2011).

Besides the natural sources of fluoride, wastewater from industries also elevates its level in ground water. The industries include brick industry, semiconductor manufacturing, electroplating, aluminum wire manufacturing, coal fired power stations, beryllium extraction industry, glass industry, ceramic industry and iron works (Shenet *al.*, 2003).

Another source of fluoride in water is artificial fluoridation of drinking water. During 1930's it was discovered that people having high fluoride level in drinking water experienced less tooth decay. After many studies fluoride addition in drinking water supply was practiced in USA in 1940s'. After the fruitful effects of fluoridation on human health this practice was continued in many countries like U.K, Canada, Australia, Japan, Spain, Brazil, Argentina and many others (Mullen, 2005).

There are about 25 countries across the world affected by fluoride poisoning. The countries that are more endemic for fluoride contamination include India, China, South Africa, Tanzania, Australia, Japan etc. (Mameriet *al.*, 1998). In Pakistan, high level of fluoride was reported in ground water of about 17 villages in east Punjab and

approximately 2.9 million people are exposed to fluoride contamination (Farooqiet *al.*, 2007).

2.3 Fluoride and Its Effects

Fluoride is important nutrient for human being. The intake of moderate amount of fluoride prevents dental caries especially among children. Fluoride modifies the process of tooth decay by three ways (Harrison, 2005):

- Enhancement in the chemical structure of the enamel
- Helps in remineralisation of enamel crystal
- Making enamel crystal more resistant to acid attack by reducing the ability of plaque bacteria to produce acid

Fluoride is stored in bones and teeth. As fluoride is electronegative element and has strong affinity with positively charged ions like calcium. The minerals in teeth are crystals of calcium and phosphate named hydroxyapatite crystals. The high chemical reactivity and small radius of fluoride allows it to displace the larger hydroxyl (OH) ion in the hydroxyapatite crystal lattice, forming fluoroapatite which increases crystal density by entering into the spaces within the hydroxyapatite crystal resulting in dental fluorosis (Meenakshi and Maheshwari, 2006).

Dental fluorosis is a defect of tooth enamel. Due to high intake of fluoride the tooth enamel losses its luster and resulted into the yellowish brown to black stains and severe pitting of teeth (Choubisa and Sompura, 1996). The high level of fluoride exposure ranging from 3 to 4 mg/L for long time is associated with skeletal fluorosis. Skeletal

fluorosis is one of the crippling endemic diseases which mainly affect the bones and skeleton of human body (Ahmad *et al.*, 2003).

Fluoride gets deposited in the joints of neck, knee, pelvic and shoulders and makes them stiff. Skeletal fluorosis is resulted in osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity. The advance stage of fluorosis is osteoporosis or bone cancer in rare cases. In some cases vertebrae, muscles and nervous system get damaged (Meenakshi and Maheshwari, 2006; Fawell *et al.*, 2006). The skeletal and dental fluorosis has no treatment and both are irreversible (Veeraputhiran and Alagumuthu, 2011).

The excessive intake of fluoride also affects the gastro intestinal tract as fluoride produces hydrofluoric acid in stomach. The fluoride is excreted via kidney and results into renal and urinary tract dysfunction. Fluoride poisoning results in the destruction of almost 60 enzymes of human body. Several researches also concluded that fluoride has the ability to interfere central nervous system, excretory system and reproductive system (Meenakshi and Maheshwari, 2006; Bhatnagar *et al.*, 2011).

According to UNEP tens of millions of people across 25 countries of both developed and developing nations are suffering from fluorosis (UNEP, 1992). The harmful effects of fluoride also prevail in Pakistan. In July 2000 a disastrous situation was reported in the area of Manga Mandi which is located at about 40 km on Multan road from Lahore, Punjab. This was for the first time highlighted in year 2000 when large numbers of affected inhabitants of the area were brought to Lahore and other cities for treatment and most of them were children. It was estimated that about 124 children of age group 4-16

years were suffering from skeletal fluorosis in that area of Manga Mandi. Fluoride level in drinking water of this area was ranging from 0.45mg/L to 29mg/L (Ahmad, 2001)

2.4 Treatment Technologies for Fluoride Removal

The following four methods are used for the removal of fluoride from drinking water (Freenstraet *al.*, 2007):

- Coagulation- Precipitation Process
- Membrane filtration processes
- Ion exchange process
- Adsorption

2.4.1 Coagulation- Precipitation Process

This method is also known as Nalgonda Technique. This technique was developed by National Environmental Engineering Research Institute (NEERI) in India. Lime (Ca(OH)_2) and alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) are used in this technique. Addition of lime leads to the precipitation of fluoride ions in the form of calcium fluoride. Precipitation is followed by coagulation by using alum. Alum is added in water with continuous stirring which resulted in insoluble aluminium hydroxide flocs formation. Then water is allowed to settle and these flocs are removed from water by electrostatic forces. Although Nalgonda is very cheap method but it has some limitations (Ayoobet *al.*, 2008; Fawellet *al.*, 2006; Eswar and Devaraj, 2011)

- Large dose of alum is required which resulted in high residual aluminum concentration in the treated water.
- Manual operation is required to operate this process

- It converts about 60-80% of fluoride into aluminum fluoride which is soluble and has toxic effect.
- Management of huge amount of sludge produced during process also make it undesirable

2.4.2 Membrane Filtration Processes

Membrane process is based on reverse osmosis (RO). RO is a physical phenomenon in which pollutants are removed by applying pressure on water to direct it through a semipermeable membrane. In this technique the contaminants are removed on the basis of size and electric charge. Reverse osmosis removes fluoride up to 98% and produces very high quality drinking water (Sehn, 2008). Nano filtration is also a type membrane having larger pores which operates at relatively low pressure and removes larger amount of fluoride as compared to RO.

Dialysis separates the solute by transport the solute from membrane. In case of dialysis membrane pores are less restrictive than nano filtration. The solute after passing through membrane separates either by Donnan dialysis or electro-dialysis (Mohapatra *et al.*, 2009). Donnan dialysis involves enrichment of trace levels of ions, metal separations through anion exchange membrane, water softening and recovery of metals from water (Hichouret *al.*, 2000). While electro-dialysis removes ionic component from ion-exchange membrane under electric field (Annouaret *al.*, 2004).

Some disadvantages of this technique are (Bhatnagaret *al.*, 2011)

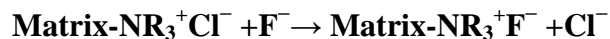
- Membrane processes are relatively expensive.
- Membrane process is susceptible to fouling and membrane degradation.

- As it removes all ions including essential mineral so remineralization is required.

2.4.3 Ion Exchange

Ion exchange is a reversible and stoichiometric processes based on the principle of exchange of loosely bound ions of firm and high molecular weight polyelectrolytes against the ions of same charge from surrounding media. For this purpose ion exchange resins are utilized. These resins are composed of a matrix, a three dimensional molecular network having chemically bonded charged functional groups (Kammereet *et al.*, 2011).

For fluoride removal basic anion-exchange resin containing ammonium functional groups is used. The reaction during this process is:



The resin containing chloride ions are replaced by fluoride ions until all the sites are occupied by fluoride. The resin can also be regenerated by washing with water containing sodium chloride. This is a very effective technique and removes up to 90% of fluoride (Meenakshi and Maheshwari, 2006).

The main disadvantages of this process are

- Other competing ions like sulphate, carbonate, phosphate reduces the removal efficiency.
- The cost of resin, waste disposal and regeneration makes the process expensive.
- Treated water contains high level of chlorides.

2.4.4 Adsorption

According to Crittenden *et al.*, 2005

“Adsorption is a mass transfer process in which a constituent in the liquid or gas phase is accumulated on solid or liquid phase and separated from its original environment”

The substance on which a constituent is accumulated is called adsorbent and the constituent that is adsorbed is known as adsorbate. During accumulation the interaction between molecules and atoms of adsorbent and adsorbate occur. On the basis of interaction between adsorbent and adsorbate there are three types of adsorption process (Kammereet *et al.*, 2011).

- Physical adsorption is a reversible mechanism in which adsorbate accumulated on the surface of adsorbent through van der Waals forces, dipole forces, dipole-dipole forces and dispersion forces.
- Chemical adsorption is a type of adsorption whereby accumulation of adsorbate onto adsorbent occurs through chemical bonding.
- Ionosorption is a type in which adsorption occurs due to ion transfer.

Adsorption is used in water treatment for the removal of organic and inorganic pollutant, heavy metals, and many color, taste and odor producing compounds (Crittenden *et al.*, 2005).

2.5 Characteristics of an Ideal Adsorbent

The efficiency of adsorbents is strongly depending on the particle size distribution, density, inner and specific surface areas and polarity. The important characteristics of an ideal adsorbent are (Kammereet *al.*, 2011; Bhatnagar and Minocha, 2006):

- Adsorbent has uniform pores structure.
- It has large surface area.
- It requires less time for adsorption equilibrium.
- It has high chemical and physical stability.

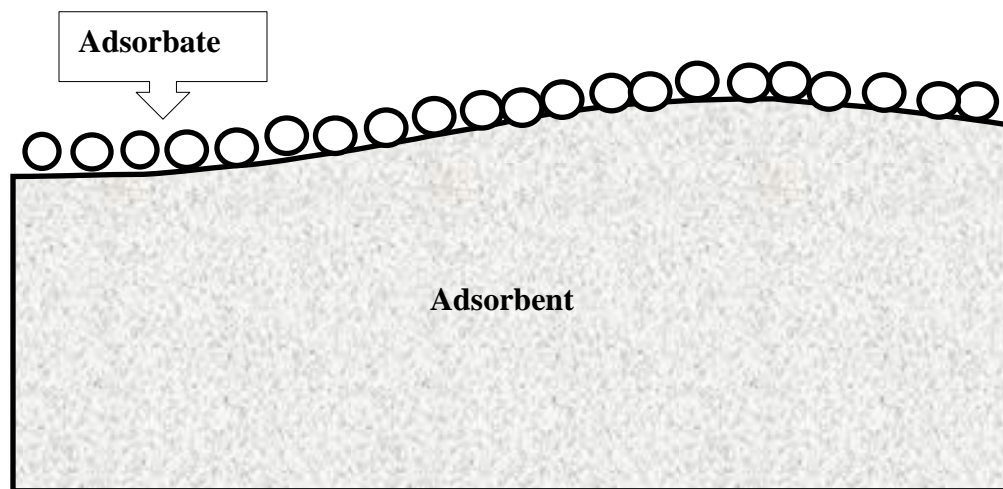


Figure 2.1: Adsorption phenomena (Qazi, 2010)

2.6 Adsorption Isotherms

Adsorption is described through isotherms. According to Adamson, 1990

“Isotherm is a function which connects the amount of adsorbate on the adsorbent with its pressure or concentration at given temperature”

There are many types of isotherms depending upon the adsorption mechanism. Some most common are Langmuir isotherm, Freundlich isotherm Temkin isotherm etc. (Alagumuthu *et al.*, 2011).

- Langmuir isotherm is applied to describe the saturated monolayer adsorption.
- Freundlich isotherm describes the adsorption onto heterogeneous surfaces.
- Temkin isotherm is applied on chemisorption.

2.7 Adsorbents for Fluoride Removal

The adsorption of fluoride on to solid adsorbent occurs in three important steps (Fan *et al.*, 2003):

- (i) Transfer of fluoride ions from solution to the surface of adsorbent.
- (ii) Adsorption of F^- on to adsorbent surfaces
- (iii) The adsorbed fluoride ions may undergo intra particle diffusion or ion exchange inside adsorbent particles.

A variety of adsorbent are used for fluoride removal from water. Some most common adsorbents are discussed here.

2.7.1 Biosorbents

Biosorption is an effective technique for fluoride removal from drinking water. Chitin and chitosan have been effectively used for defluoridation. Kamble *et al.*, 2007 used 20% lanthanum chitosan for fluoride removal. He observed that maximum removal was achieved at neutral pH while in acidic and alkaline conditions the removal efficiency decreased.

Yao *et al.*, 2009 also employed chitosan modified with neodymium for the removal of fluoride. It was evaluated that the efficiency of modified chitosan was strongly affected by pH and temperature. Algal biomass was also used as adsorbent. Mohan *et al.*, 2007 used algal *Spirogyra* as adsorbent. The fluoride removal efficiency was found to be 54% with the adsorption capacity of 1.3mg/g.

Some low cost biosorbents have also been used for excessive fluoride removal. Fresh leaves of Neem (*Azadirachta indica*), Pipal (*Ficus religiosa*) and Khair (*Acacia catechu willd*) trees were chosen and undergone a long process of preparation by crushing, sun drying, followed by heating and washing. The fluoride removal efficiency was found to be 80% at 12g/L of adsorbent dose (Jamode *et al.*, 2004). Similarly Harikumare *et al.*, 2012 did defluoridation study using aherbal plant Vetiver (*Vetiveria zizanioides*) that resulted into 80 % removal at adsorbent dose of 1g per 50 mL of fluoridated water.

2.7.2 Low Cost and Natural Adsorbents

Various naturally occurring material available abundantly are also used for defluoridation. Sun *et al.*, 2011 utilized iron (Fe^{3+}) modified stilbite zeolite. The fluoride adsorption was well described by Langmuir model and maximum adsorption capacity was 2.3 mg/g at initial fluoride concentration of 10mg/L.

Gogoi and Baruah, 2008 used acid activated kaolinite clay for fluoride removal. Similarly Meenakshi *et al.*, 2008 did fluoride adsorption study using mechanochemically activated kaolinite having adsorption capacity of 0.8 mg/g. Thakreet *et al.*, 2010 prepared bentonite clay containing magnesium for defluoridation which gave 2.3 mg/g adsorption capacity at initial concentration of 5 mg/L of fluoride.

Both agriculture and industrial waste are used as sorbent for defluoridation. These adsorbents are very economical, and renewable in nature. Nigussieet *et al.*, 2007 removed excess of fluoride by waste residues of alum manufacturing. The removal efficiency of waste residues was about 85% at initial concentration of fluoride 10 mg/L.

2.7.3 Bone Charcoal

Bone char is the oldest water defluoridation agent. It is blackish in color and granular in form. It contains 57-80% calcium phosphate, 6-10% calcium carbonate and 7-10% activated carbon. Bone charcoal has been prepared from the bones of many animals like dogs, pig, cattle, fish etc. (Fawellet *et al.*, 2006). In a study fish bone charcoal was successfully used in the form of column for fluoride removal at domestic level. The main focus of the study was on the economical treatment of fluoride in drinking water. The removal capacity of fish bone charcoal was between 0.3 to 1.4 mg/g but the removal

capacity is inversely proportional to the flow rate of column and directly proportional to the initial fluoride concentration (Bhargava, 1997).

Bone charcoal has been regenerated both chemically and thermally. Kaseva (2006) used regenerated bone charcoal for defluoridation. Regeneration was carried out by heating bone charcoal at 500°C for 120 minutes of optimum time. The removal efficiency of the regenerated bone charcoal was about 71%. There are some disadvantages of using bone charcoal as an adsorbent such as (Fawellet *al.*, 2006).

- It is difficult to predict its saturation and requires continuous monitoring.
- At high flow rate removal efficiency decreases.
- If bone charcoal is not properly prepared, the water treated may taste and smell like rotten meat.
- Its packing in column is less convenient to use.

Watnask and Watnask (2000) compared the sorption behavior of fluoride on bone charcoal and activated carbon. He observed that the sorption equilibrium time for activated charcoal was 15 minutes while bone charcoal required 5 hours. He also observed that activated charcoal is five times more convenient to use than bone charcoal.

2.7.4 Activated Charcoal

Activated charcoal is hydrophobic and was first time used in the sugar industry in England in 1794 to decolorize sugar syrup. Its contribution to clean environment was initiated during First World War for use in filters to remove chemical agents from air (Yang, 2003). Activated carbon has exceptionally high surface area. Just one gram of

activated carbon has surface area about 500m^2 . The three types of activated carbon are granular, powder and pellets. Due to its versatile surface chemistry and highly developed porosity it is considered as a universal adsorbent. Activated carbon has vast application in industries, food production, medicines etc. (Bansal and Goyal, 2005).

Activated carbon derived from different sources is used as adsorbent for fluoride removal from drinking water. Activated carbon prepared from peels of different fruits has been used very effectively for defluoridation (Chakrapani *et al.*, 2010).

Tembhurkar and Dongre, 2006 studied the suitability of activated carbon for defluoridation. The commercially available activated charcoal has 94% fluoride removal efficiency within the contact time of 120 minutes. The optimum dose of activated charcoal for the study was $0.2\text{g}/100\text{mL}$ and optimum stirring rate was 60rpm.

Kumar *et al.*, 2008 prepared the activated carbon from neem and keekar leaves thermally and used them for fluoride removal from drinking water. It was observed that adsorption capacity of both adsorbents named thermally activated keekar leaves and thermally activated neem leaves carbon were highly dependent upon the pH, dose and particle size of adsorbent. Both adsorbents followed Freundlich isotherm model.

Veeraputhiran and Alagumuthu in 2011 prepared naturally occurring and low cost activated carbon from *Phyllanthusemblica*, a type of seed for fluoride removal. Maximum removal obtained was 82 % for the initial fluoride concentration 3 ppm and adsorbent dose of 0.7 g at room temperature and neutral pH.

Activated charcoal modified with other elements was also used by the researchers for defluoridation studies. Tchomgui- Kamga *et al.*, 2010 prepared activated charcoal that

contain aluminum oxide and iron oxide by impregnating wood with salt solution followed by heating at high temperature for carbonization. The carbon prepared was found to be highly porous and more than 92% removal was achieved within 24 hours at initial fluoride concentration of 10 mg/L.

2.7.5 Activated Alumina

Activated alumina is a porous solid structure manufactured by thermal treatment of aluminum hydroxide. Activated alumina has the surface area of $200\text{m}^2/\text{g}$. It is a versatile adsorbent and has been utilized successfully for the removal of fluoride (Bhatnagar and Minocha, 2006). Activated alumina is the favorable technique in case high removal efficiency and high capacity is needed (Freenstraet *al.*, 2007). The adsorption of fluoride by activated alumina is highly dependent on the contact time, pH and adsorbent concentration. Moreover activated alumina can remove many other toxic elements that often coexist with fluoride in groundwater, including arsenic and selenium (Ghorai and Pant, 2005).

In order to increase the removal efficiency the activated alumina was supported with carbon nano tubes which resulted in 4 times more efficient than activated alumina at equilibrium fluoride concentration of 12mg/L (Li *et al.*, 2001). Louniciet *al.*, 2004 studied the fluoride removal by using electro-activated alumina. The study was done by using electric field to activate the alumina. Although the ionic strength of activated alumina was increased but it did not has considerable effect on the adsorption capacity of alumina.

In another study Viswanathan and Meenakshi, 2010 increased the defluoridation capacity of alumina by preparing alumina chitosan composites by incorporating alumina particles in the chitosan polymeric matrix. Alumina chitosan composites are 2.4 times more efficient than pure activated alumina for fluoride removal.

Tripathy *et al.*, 2006 investigated the ability of activated alumina impregnated with alum (AIAA) for fluoride removal. The experiments were done in batch mode in order to study the effect of parameters like pH, adsorbent dose, and initial fluoride concentration. The removal efficiency was found to be 99% at neutral pH within 3 hours at initial concentration of 20mg/L of fluoride found in 50 mL test solution and adsorbent dose was 8 g/L. The study also revealed that exhausted AIAA can be reused by acid-base rinsing procedure.

Commercially available adsorbents are fine powders. Such adsorbents cannot be used conveniently for water treatment because their separation and recycling is difficult and costly. Therefore granulation is a convenient method to produce granules with high mechanical stability and appropriate for practical application. A study on the granulation of a nano adsorbent by immobilization in porous polyvinyl alcohol for defluoridation was conducted. The adsorption capacity of the granules was 4.46 mg/g at initial fluoride concentration of 19 mg/L (Wu *et al.*, 2011).

Maliyekka *et al.*, 2008 studied the fluoride removal using activated alumina granules containing magnesium (MAAA). MAAA was prepared by calcination of magnesium hydroxide impregnated activated alumina at 450°C. Scanning Electron Microscopy (SEM) and X-ray powder diffraction (XRD) were done in order to

characterize the physicochemical properties of MAAA. The 95% removal was achieved within contact time of 3 hours at initial concentration of fluoride 10 mg/L at neutral pH. But impregnated granules require filtration for the removal from test solution after adsorption.

The textural features and pore size of activated alumina was improved by preparing mesoporous alumina using aluminum tri-sec-butoxide in the presence of either cetyltrimethylammonium bromide or stearic acid. These mesoporous alumina have surface area of 421 or 650m²/g which resulted in increased adsorption capacity of 2.2 or 45 times more than commercially available activated alumina (Lee *et al.*, 2010).

2.7.6 Sol- Gel Derived Activated Alumina

The sol-gel derived alumina granules offer more advantages than alumina granules prepared from conventional method. The precursor of sol-gel derived alumina is aluminum tri sec butoxide which is supposed to produce granules having high surface area. Sol-gel derived alumina has excellent mechanical strength, low attrition rate, high thermal and chemical stability and uniform pore size distribution (Wang and Lin, 1998).

Buelna and Lin, 1999 prepared the sol-gel derived alumina by using different precursors. They found that good quality alumina granules can be prepared from aluminum tri-sec butoxide, aluminum isopropoxide and catapal boehmite powder. They also observed that alumina granules prepared from these precursors under sol-gel method were better than commercially available alumina granules. Another finding of the study was that pore structure of sol-gel derived AA was strongly depending on the type of precursor and concentration of acid used.

Deng *et al.*, 2006 also prepared sol-gel derived alumina by using Yolda's method. They observed that the prepared adsorbent could effectively remove not only fluoride but also arsenic from drinking water. Lucy *et al.*, 2010 did further advancement in the technique by modifying sol-gel derived alumina granules with calcium oxide and manganese oxide. The calcium oxide-modified activated alumina showed higher fluoride adsorption capacity than manganese oxide-modified alumina and pure sol-gel derived activated alumina. It was also observed that external and intraparticle diffusion contribute to the removal efficiency of sol-gel derived alumina.

MATERIALS AND METHODS

This chapter describes the materials and equipment used and methodology adopted for the research work.

3.1 Materials

Chemicals used in the present study include TISAB and SPADNS reagent(Hach, USA), aluminum-tri sec butoxide , activated alumina and sodium fluoride (Merck, Germany), alum and nitric acid 65% (Panreac , Spain), paraffin oil (MP Biochemicals, Germany), ammonia solution 33% (Burdick and Jackson, Germany) and activated charcoal (Acros Organics, USA).

3.2 Instruments

3.2.1 Ion Selective Electrode (ISE)

Ion selective electrode (ISE) is widely used for the potentiometric determination of ionic species. ISE is worked on principle of passage of charge species from one phase to another produces a potential which is proportional to the amount or concentration of the analyte. It is more advantageous than other techniques as it is easy to use and measurement is very fast. It can be used over a wide range of concentration and considerably less expensive (Mendham *et al.*, 2006).

The potential difference of ion-sensitive membrane is:

$$E = K - (2.303RT/nF) \log (a)..... (3.1)$$

Where, K is a constant for all other potentials, R is gas constant, T is temperature, n is the number of electrons that are transferred, F is the Faraday's constant, and a is the activity of the analyte ion. A plot between $\log(a)$ and potential measured will give a straight line (Noh, 2005).

The ISE consist of a reference electrode, a sensing electrode and a potential measuring device (voltmeter). The reference electrode provides electrical potential that is required to compare with the sensing membrane potential. It also contains filling solution that completes the electrical circuit between the internal cell of the reference electrode and sample. The sensing electrode is also called ion selective electrode because of its selective reactivity with analyte (Noh, 2005).

In the present study, Ion Meter Model 25 Hach, USA ISE is used to detect fluoride concentration before and after adsorption. The fluoride electrode consists of a solid state inorganic membrane of LaF_3 crystal which is enclosed into an epoxy body. The Fluoride ISE is susceptible to interferences of other ions. Total Ionic Strength Adjustment Buffer (TISAB) is used to solve this problem (Barabas, 1975). The function of the TISAB is:

- Adjustment of a constant ionic strength for standards and samples
- Maintaining the pH of solution at 5.00 to eliminate the effect of pH changes.
- De-complexation to release any fluoride ions which may be bound up in complex molecules.

The TISAB solution contains 1.0 M NaCl, 0.25 M acetic acid, 0.75 M sodium acetate, and 0.01 M sodium citrate (Crompton, 2002).

3.2.2 Spectrophotometer

A spectrophotometer is used to measure the amount of light that a sample absorbs. Light of specific wavelength that consists of photons is passed through the sample. The analyte molecules absorb photons. This absorption reduces the number of photons and finally the intensity of light. The working of the spectrophotometer is based on the Beer-Lambert Law (George, 1997).

For the analysis of fluoride by spectrophotometer, SPADNS method is used. This method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with dye, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}) and the dye. As the amount of fluoride increases, the color produced becomes lighter. For this method spectrophotometer is set at 570 nm which provided the light path of at least 1cm (APHA, 2005). In the present study, DR2010, Hach USA spectrophotometer was used.

3.2.3 Scanning Electron Microscope (SEM)

The scanning electron microscope is a scientific instrument that uses a beam of high energy accelerated electrons to generate signals at the surface of specimen. These signals reveal information about the external morphology, chemical composition and crystalline structure of the sample. A SEM has following components (Danilatos, 1988):

- Electron Gun
- Electron Lenses
- Sample storage
- Detectors

- Data output devices

JEOL JSM-6460, Japan SEM was used in the present study to check the surface of the modified immobilized activated alumina before and after adsorption and also after thermal regeneration.

3.3 Methodology

3.3.1 Preparation of Immobilized Activated Alumina by Sol-Gel Method

The immobilized activated alumina was prepared by using sol-gel method. The sol of activated alumina was named as Boehmite sol (γ -ALOOH). Boehmite sol was synthesized by dissolving drop wise 100ml aluminum tri sec butoxide in 300 mL distilled water at 75°C on a heat stirrer. After dissolution, the solution was heated at 90°C for one hour and 15 ml 1M HNO₃ was added in the slurry containing boehmite sol precipitates.

To obtain stable boehmite sol, the resulting slurry was subjected to closed reflux in water bath at 90°C for 10 hours. After reflux the sol was dried in a petri dish at 40°C in oven. The semi liquid gel was dropping by using a syringe without needle in the ammonia solution having a top layer of paraffin oil. The droplets were remained in this solution for 45 minutes for aging. During aging ammonia neutralized the acid inside the partially gelled particles by penetrating into the particles. Thus, the wet gel granules were aged and became solid granules.

After that the solid granules were withdrawn from the solution in sieve and washed thoroughly by using distilled water and ethyl alcohol to remove most of the oil. The granules were then dried and calcined at 450°C in muffle furnace for three hours to

obtain stable activated alumina. For each batch adsorption experiment fresh adsorbent was prepared as the stated amount is enough for one batch test.

3.3.2 Adsorption Trial of Sol Gel Derived Immobilized Alumina

In order to check the removal efficiency of sol gel derived immobilized alumina batch adsorption experiments were performed. A supposed dose of adsorbent 0.5 g was added in 100 mL test solution containing initial fluoride concentration of 5 mg/L. It was followed by the agitation of test solution at 150 rpm for 90 minutes of contact time. The temperature of adsorption experiments was $20 \pm 1^\circ\text{C}$. After 90 minutes the supernatant was taken from the test solution which was subjected to analysis by using ISE and spectrophotometer.

3.3.3 Modification of Immobilized Alumina

In order to increase the efficiency of immobilized alumina, it was aimed to add any other adsorbent in it. For this purpose, three adsorbents were selected and tested their efficiency of fluoride removal alone. The three adsorbents were

- Activated Charcoal
- Zeolite
- Alum

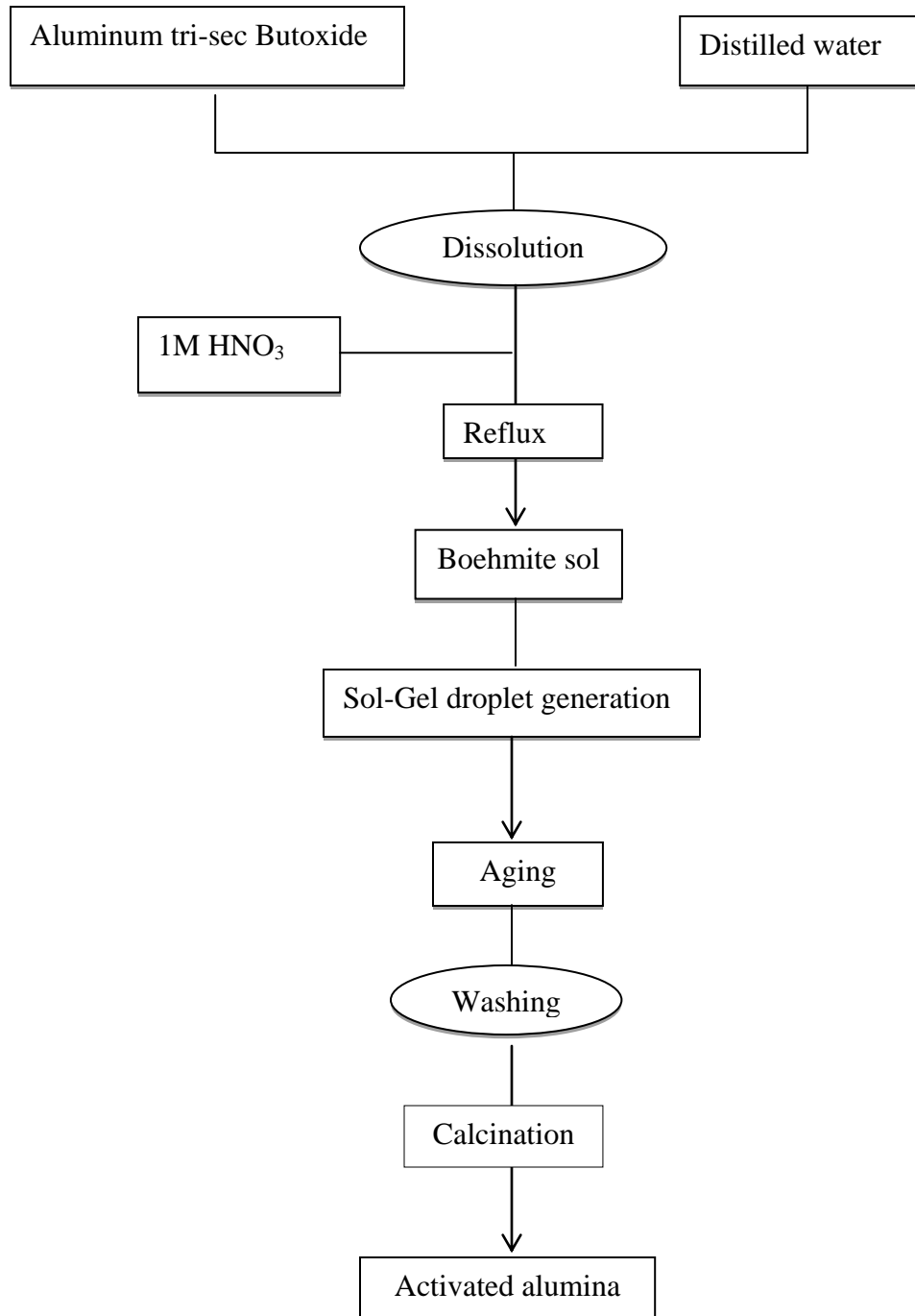


Figure 3.1: Sol-Gel method of activated alumina(Deng *et al.*, 2011)

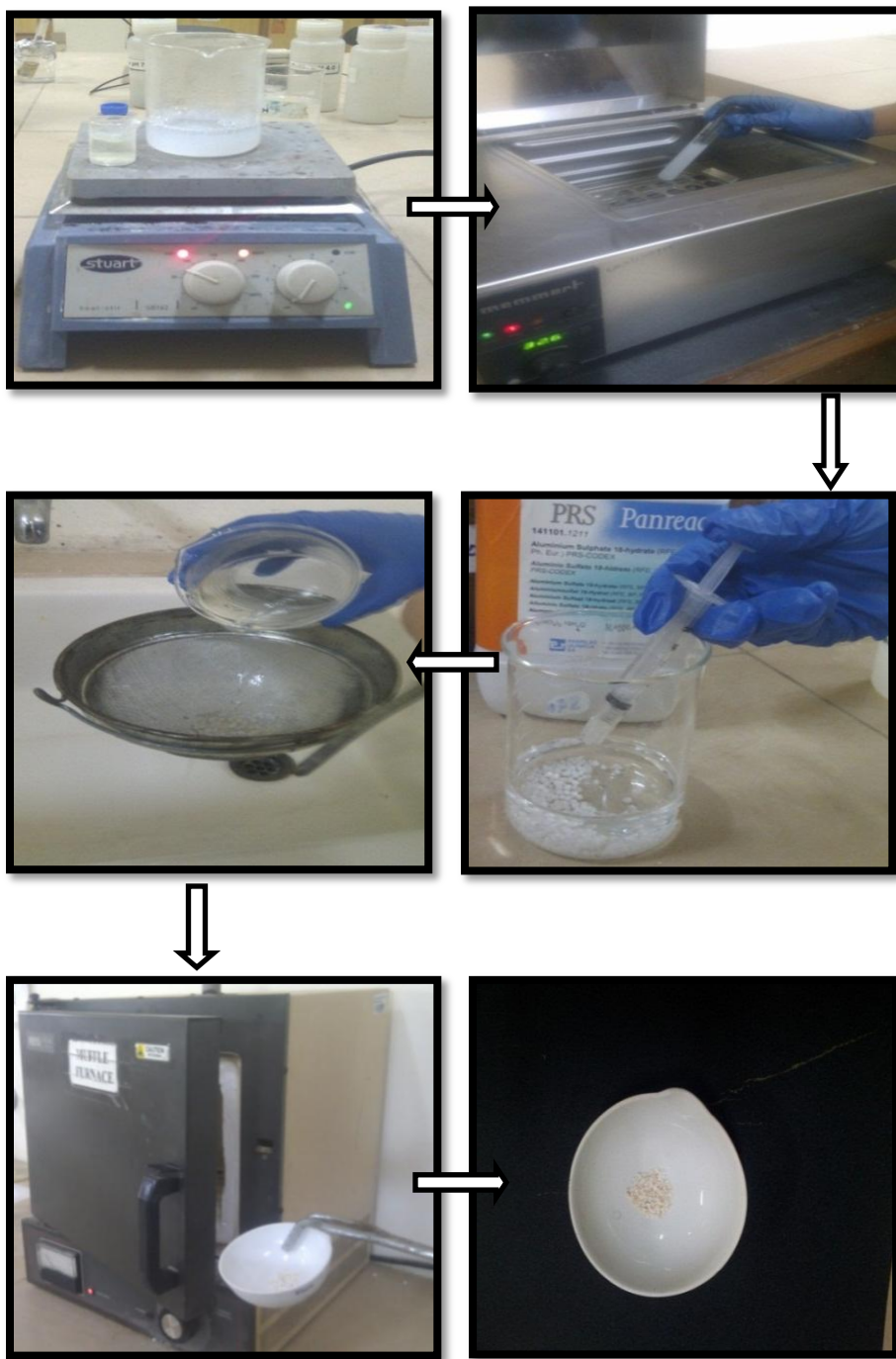


Figure 3.2: Pictorial view of Sol-Gel method

On the basis of fluoride removal efficiency, activated charcoal and alum were chosen and added separately in the sol gel method right from the start of the dissolution. For this purpose we add different amount of alum and charcoal with 5ml aluminum tri-secondary butoxide, 15 mL distilled water and 0.77 mL HNO₃. From these two, alum with the amount of 0.5 g was mixed well with sol gel derived alumina and enhances defluoridation efficiency than activated charcoal. The new adsorbent was prepared with same proportion as 10 g alum was added in the 100 mL tri-sec butoxide and 300ml distilled water then subject to sol gel procedure. The new adsorbent was named as Modified immobilized Activated Alumina (MIAA).

3.4 Adsorption Study

Fluoride adsorption experiments were employed in order to determine the efficiency of adsorbent and the effect of controlling parameters like dose, contact time and stirring rate. The stock solution of 5mg/L of fluoride was prepared by dissolving 0.011 g of reagent grade NaF in 1000mL distilled water. All adsorption experiments were carried out in a 250 mL conical flask with 100 mL test solution at room temperature (20^o±1^oC) using a mechanical shaker. The pH of the test solution was remained neutral in order to maintain drinking water conditions. Fluoride ion concentration was measured by using both spectrophotometer and ion selective electrode. A triplicate batch experiment was run in order to check the precision.

3.4.1 Effect of Adsorbent Dose

The effect of an increase in the dose of adsorbent on fluoride removal was being studied by varying the dose from 0.5 up to 20 g/L in test solution containing initial fluoride concentration of 5 mg/L.

3.4.2 Effect of Contact Time

In order to determine the equilibrium adsorption time, the flasks containing test solution of fluoride with optimum adsorbent dose, were agitated on the shaker for periods of 5, 15, 30, 45, 60, 75, 90 and 120 minutes.

3.4.3 Effect of Stirring Rate

Optimum stirring rate, the adsorption experiment was carried out by changing rpm ranging 50 to 250 of mechanical shaker.

3.4.4 Effect of Varying Initial Fluoride Concentration

The effect of varying concentration of fluoride concentration was also studied by changing the concentration from 0.5 to 12 (mg/L). The specified amount of fluoride adsorbed q_e (mg/g) was calculated by eq (3.2)

$$q_e = \frac{C_i - C_s}{m} \dots\dots\dots (3.2)$$

Where C_i is the initial fluoride concentration (mg/L), C_s is the residual fluoride concentration at equilibrium (mg/L) and m is the mass of adsorbent in test solution (g/L).

3.4.5 Isotherm Study

“Adsorption isotherm is the relationship between the amount of substance adsorbed and its concentration in equilibrium solution at constant temperature.”

In the present study, Langmuir and Freundlich isotherm was used to explain the adsorption study. Freundlich is most commonly used isotherm for describing multilayer adsorption with possible interaction between adsorbed molecules (Dan *et al.*, 2011).

The equation for the linear form of the Freundlich is

$$\text{Log } q_e = \frac{1}{n} \text{Log } C_s + \text{log } K_f \dots \dots \dots (3.3)$$

Where,

q_e = amount of fluoride adsorbed per unit mass of adsorbent

C_s = equilibrium concentration of fluoride

K_f = adsorption affinity

n = heterogeneity of adsorbent

The values of $1/n$ and k_f were directly obtained from slope and intercept of the linear plot between $\log q_e$ and $\log C_s$.

The Langmuir isotherm is most commonly observed isotherm that is applied to describe the monolayer adsorption. Langmuir isotherm is only applied to the adsorption systems in which the solid adsorbent has limited adsorption capacity (q_e), all active sites are similar and one active site can only combine with one adsorbate molecule (Dan *et al.*, 2011)

The equation for Langmuir isotherm is

$$\frac{C_s}{q_e} = \frac{C_s}{V_m} + \frac{1}{KV_m} \dots \dots \dots (3.4)$$

Where,

q_e = amount of fluoride adsorbed per unit mass of adsorbent

C_s = equilibrium concentration of fluoride

K = adsorption affinity

V_m = maximum adsorption capacity

The values of K and V_m were directly obtained from intercept and slope of the linear plot between q_e and C_s .

3.4.6 Comparison with other Adsorbents

In order to compare the efficiency of MIAA for fluoride removal from drinking water two other analytical grade adsorbents were used which were:

- Activated charcoal
- Activated alumina

Both adsorbents were in powdered form. The experimental steps described in section 3.4.1 to 3.4.5 were carried out for these adsorbents as well. But for these adsorbents required settling of about 10 minutes and then filtration after constant shaking for specified contact time period. Filtration was done by using ordinary whatman filter paper.

3.5 Regeneration of MIAA

In order to check multi time usage of MIAA, regeneration of MIAA was done both thermally and chemically. Before regeneration the exhausted adsorbent was washed properly with distilled water and dried at room temperature. For thermal regeneration the adsorbent was heated in muffle furnace for 30 minutes at 450°C. In case of chemical regeneration, exhausted adsorbent was soaked in 0.1 M NaOH solution for two hours. After the specified time, the adsorbent was washed with distilled water until the washed water pH become neutral.

3.6 Real Water Sample Study

Adsorption experiments using MIAA were employed on 5 drinking water samples (A-E) collected from fluoride affected area of Manga Mandi near Lahore by random sampling.

RESULTS AND DISCUSSION

4.1 Modified Immobilized Activated Alumina

The removal efficiency of sol-gel derived non modified activated alumina was 70% at initial fluoride concentration of 5 mg/L with adsorbent dose of 5 g/L. Since 70% removal was not that high therefore modifications in the immobilized activated alumina were made in order to increase its adsorption capacity. For this purpose, three additives named activated charcoal, alum and zeolite were selected to be incorporated in immobilized activated alumina and their removal efficiency was tested separately.

The results revealed that activated charcoal gave 80 % removal, zeolite 1% and alum 20% removal. Based on the percentage removal activated charcoal and alum were selected to be used as additives for modification of immobilized activated alumina. Equal amounts of activated charcoal and alum were added during the preparation of sol at dissolution step and studied their removal efficiency after the preparation of modified adsorbent.

The results of both additives' removal efficiency at different amounts were depicted in Table (4.1). The results of activated charcoal showed that granules were burnt during calcination and then disintegrate in the test solution used for adsorption study. This may be due to the high temperature (450°C) and presence of oxygen in muffle furnace during calcination.

The disintegration of granules revealed that molecules of activated charcoal do not have affinity with sol gel derived alumina. But in case of alum, the amount of 0.5g gave maximum removal and selected as optimized amount for further preparation of immobilized adsorbent that was named modified immobilized activated alumina (MIAA).

The general appearance of MIAA was white hard granules. The SEM images of MIAA before and after adsorption showed that there was a considerable change in the surface of adsorbent after adsorption as fluoride ions were considered to adhere on the MIAA, refer Figure 4.1(A, B and C).

Table 4.1: Adsorbents and % removal of fluoride

Adsorbents	% Removal of F⁻
Activated Charcoal	80
Zeolite	1
Alum	20

Table 4.2: Amount of adsorbents and their adsorption efficiency

Activated Charcoal		Alum	
Amount (g)	F⁻ adsorption efficiency	Amount (g)	F⁻ adsorption Efficiency
0.25	Burned, granules break	0.25	80 % F ⁻ removal
0.5	Same as above	0.5	85 % removal
2.5	Same as above	2.5	60% removal, granules break



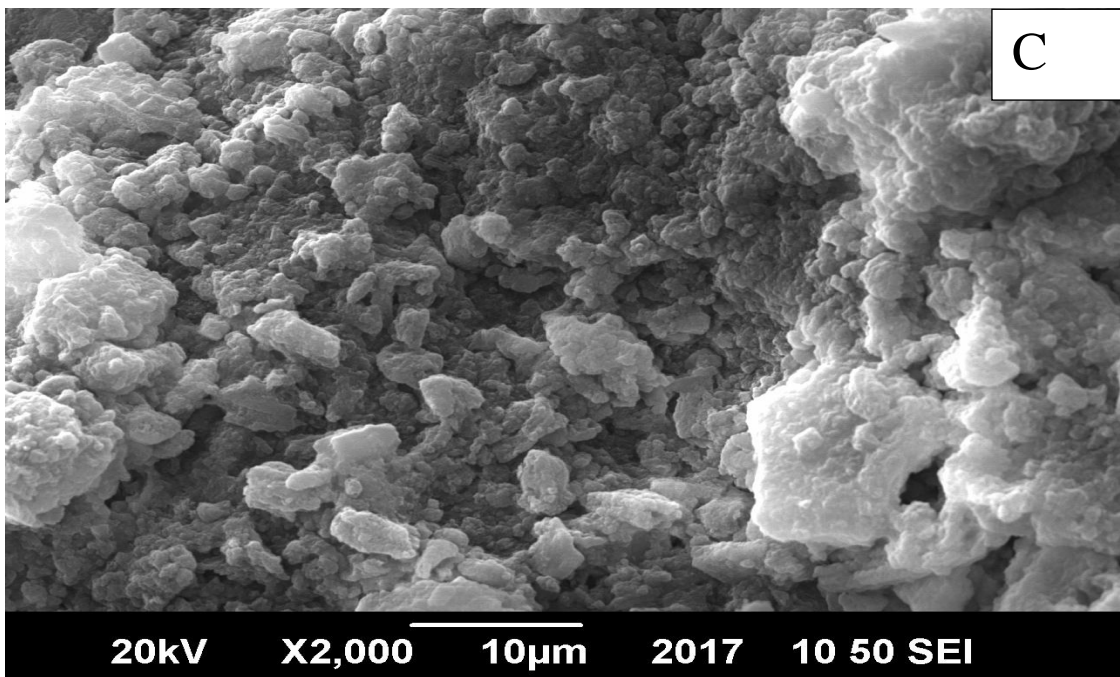
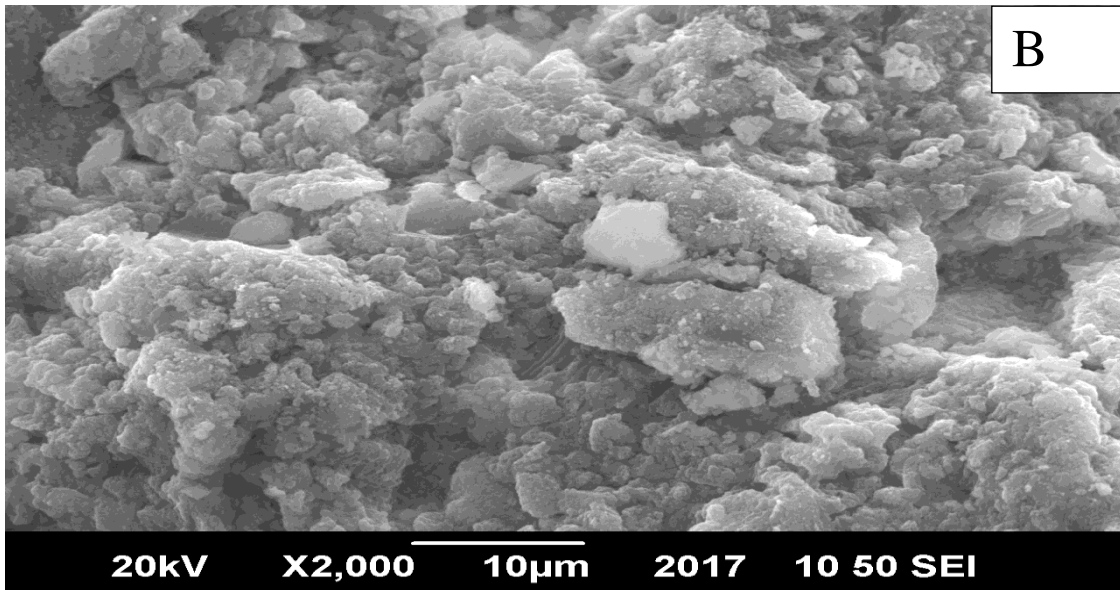


Figure 4.1: (A) MIAA granules, SEM image of MIAA (B) before adsorption, (C) after adsorption.

4.2 Effect of Adsorbent Dose

The effect of adsorbent dose of three adsorbents modified immobilized activated alumina (MIAA), activated charcoal (AC) and activated alumina (AA) on the removal of fluoride at initial fluoride concentration of 5 mg/L for 90 minutes was shown in figure 4.2 (a, b and c). All of the three adsorbents showed similar trend for fluoride removal. MIAA reaches to 95% at dose of 10 g/L after this there is no significant increase in the fluoride removal. In case of AC 89% removal attains at 10 g/L and for AA the fluoride removal is 90% at 10 g/L.

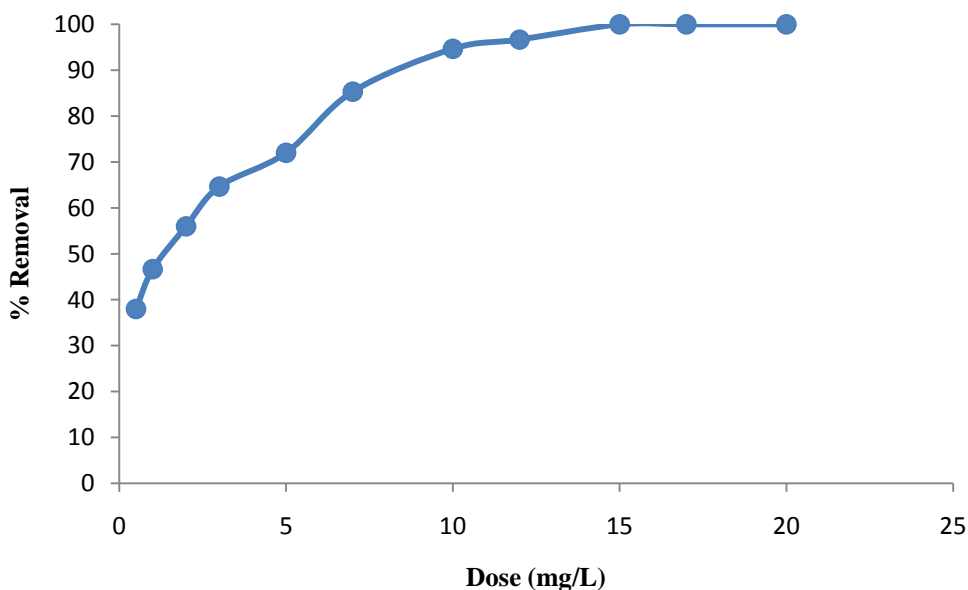
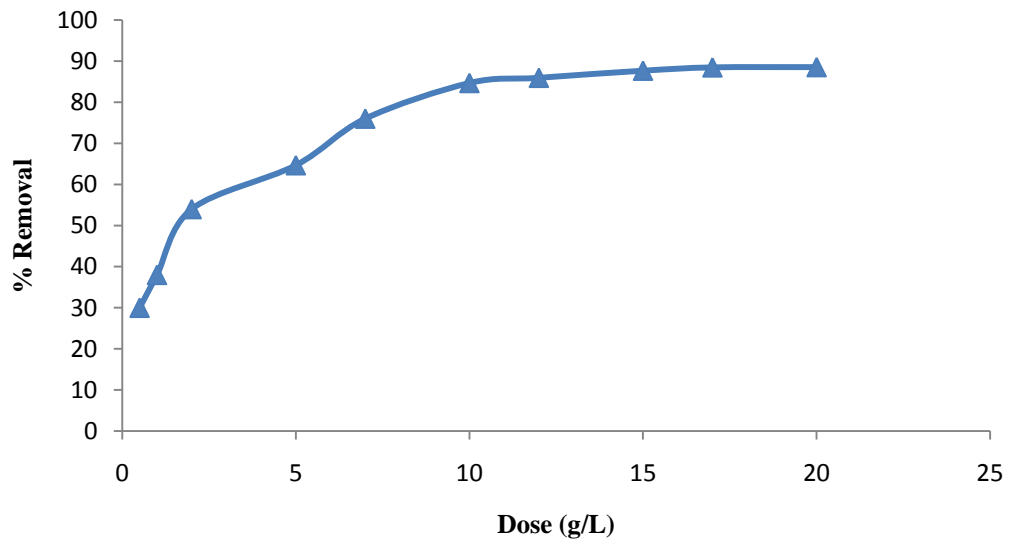
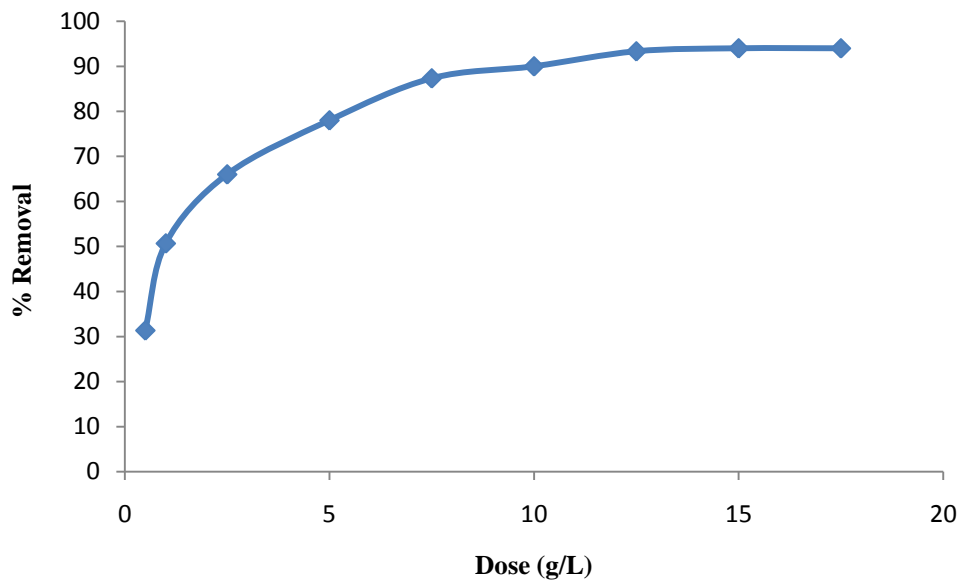


Figure 4.2 (a): Effect of adsorbent dose and removal efficiency of MIAA at(20±1 °C)



**Figure 4.2(b): Effect of adsorbent dose and removal efficiency of ACat
(20±1 °C)**



**Figure 4.2(c): Effect of adsorbent dose and removal efficiency of AA at
(20±1 °C).**

4.3 Effect of Contact Time

The progression of adsorption process at different contact time is shown in Figure 4.3 (a, b and c). As the contact time increased the adsorption capacity of three adsorbents (MIAA, AC and AA) also increased. The adsorption process assumes to occur in three phases. The increase in the adsorption capacity of three adsorbents in first phase was very rapid with the contact time of 20 minutes. In this phase adsorption of fluoride may be due to the diffusion takes place into the pores on the surface of the adsorbent. In the second phase adsorption capacity decreased due to the migration of fluoride ions from upper surface to inner pores. In the last phase, the MIAA and AA removed most of the fluoride after 60 minutes and then attained equilibrium but in case of activated charcoal adsorption capacity reached to equilibrium after 90 minutes. In another study of fluoride adsorption by activated alumina same equilibrium contact time was observed (Srimurali and Karthikeyan, 2008).

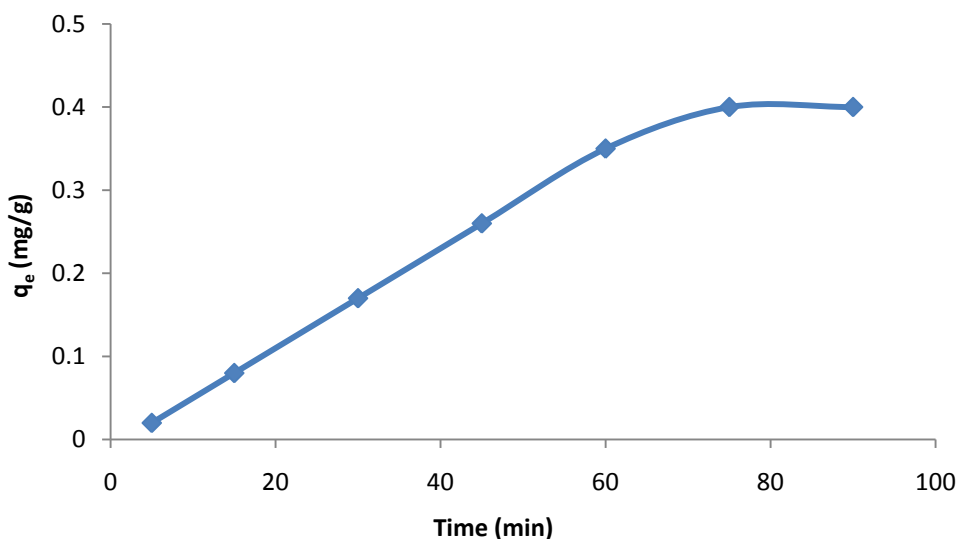


Figure 4.3(a): Effect of contact time on adsorption capacity of MIAA at (20 ± 1) °C

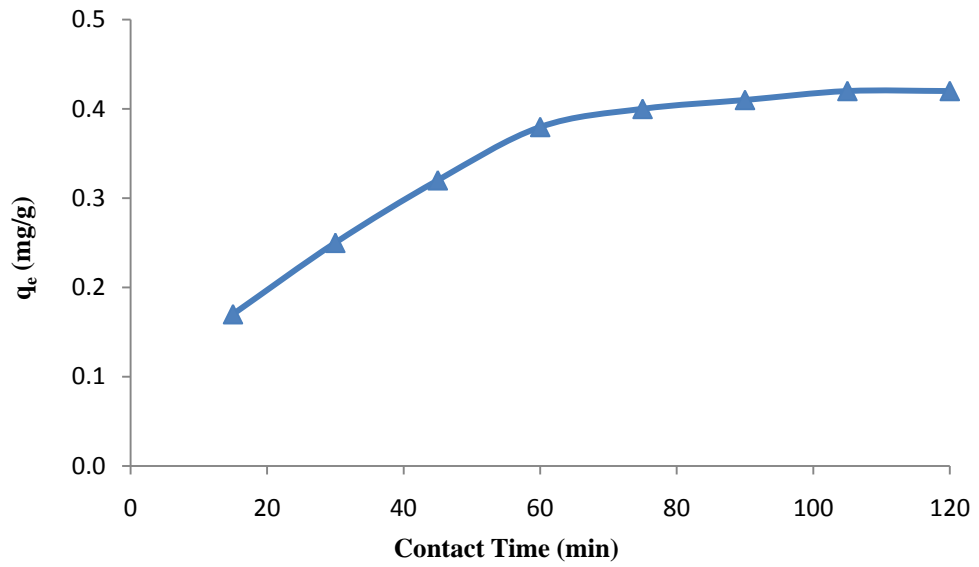


Figure 4.3(b): Effect of contact time on adsorption capacity of AC at ($20 \pm 1^\circ\text{C}$)

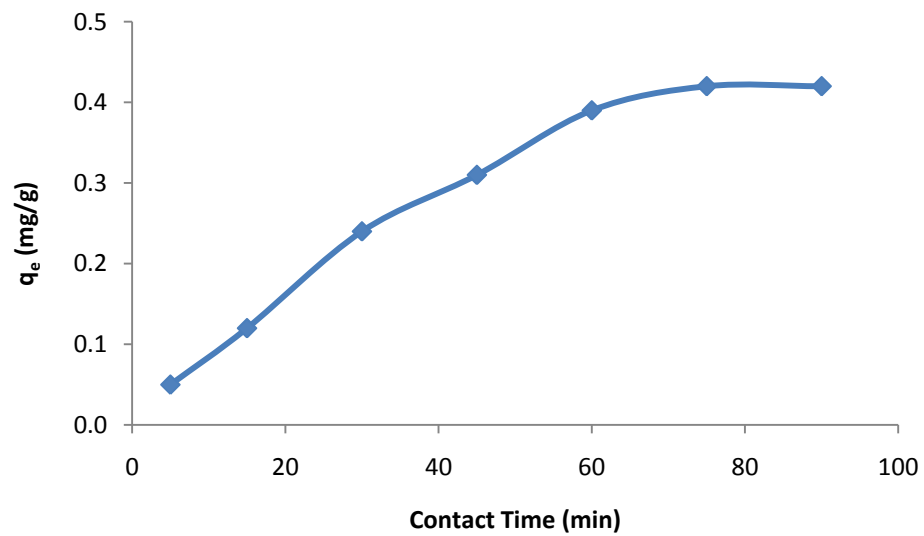


Figure 4.3(c): Effect of contact time on adsorption capacity of AA at ($20 \pm 1^\circ\text{C}$)

4.4 Effect of Stirring Rate

The influence of stirring rate on adsorption phenomena is shown in Figure 4.4 (a, b and c). Stirring rate has significant effect on the extent of adsorption and it revealed that fluoride removal was a function of stirring rate. At a given time, fluoride removal increases with the increase in the rate of stirring. In case of MIAA the adsorption capacity was 0.02mg/g and attained 0.4mg/g at 150 rpm, while in case of activated charcoal and activated alumina equilibrium condition attained at 100 rpm with the adsorption capacity of 0.4mg/g and 0.44mg/g respectively. The reason for increase in adsorption capacity with increase in the stirring rate was that at higher speed better contact between the adsorbate and adsorbent is possible (Killedar and Bhargava, 1993).

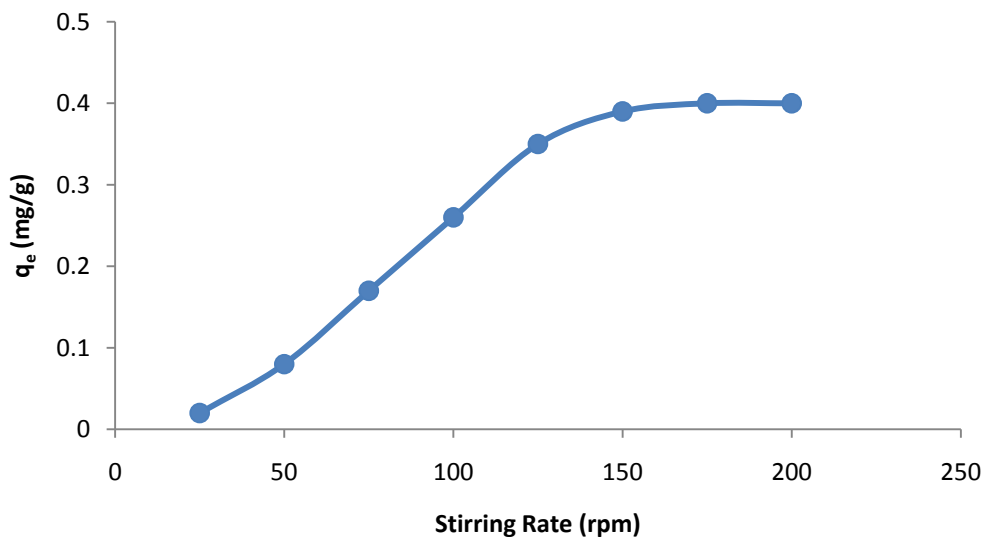


Figure 4.4(a): Effect of stirring rate on adsorption capacity of MIAA at (20±1 °C)

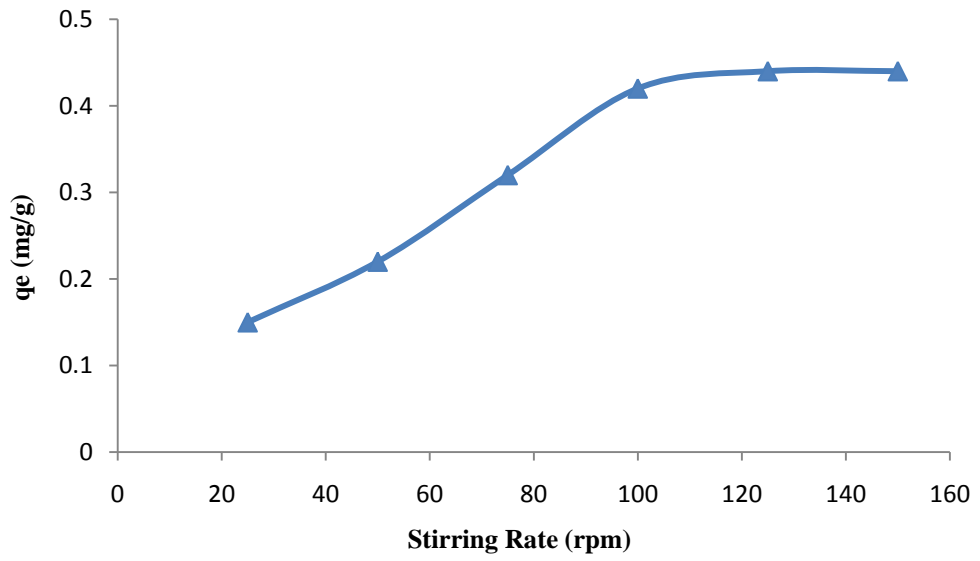


Figure 4.4(b): Effect of stirring rate on adsorption capacity of AC at (20±1 °C)

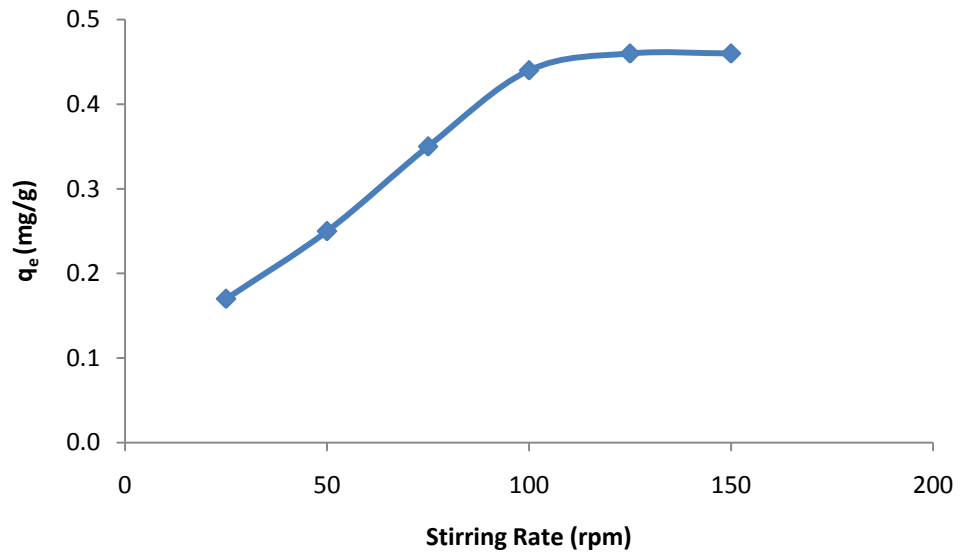


Figure 4.4(c): Effect of stirring rate on adsorption capacity of AA at (20±1 °C)

4.5 Effect of Initial Fluoride Concentration

The effect of increasing Fluoride concentration on adsorption capacity of MIAA, activated charcoal and activated alumina was shown in figure 4.5 (a, b and c). In case of all three adsorbents the adsorption capacity increased to a specified level then attained equilibrium. The maximum adsorption capacity of MIAA was 0.76mg/g, activated charcoal was 0.47mg/g and activated alumina 0.6mg/g at initial fluoride concentration of 12mg/L.

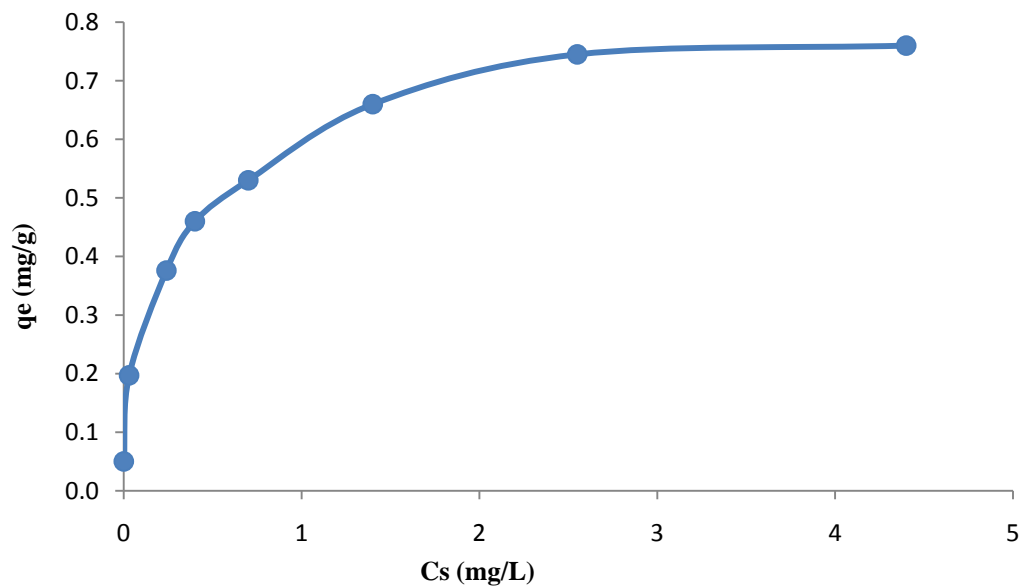


Figure 4.5(a): Effect of initial concentration of fluoride on adsorption capacity of MIAA at (20±1 °C)

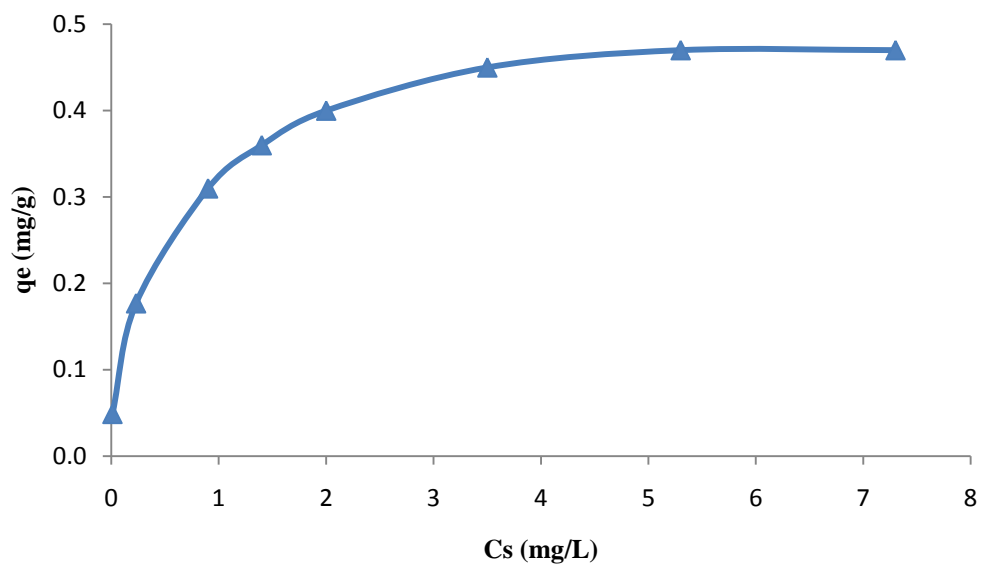


Figure 4.5(b): Effect of initial concentration of fluoride on adsorption capacity of AC at (20±1 °C)

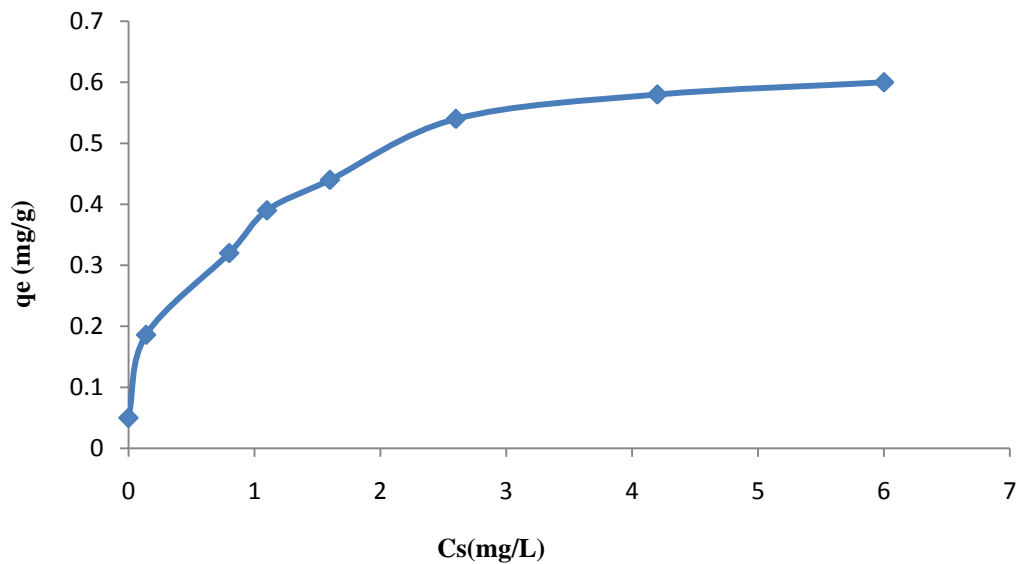


Figure 4.5(c): Effect of initial concentration of fluoride on adsorption capacity of AA at (20±1 °C)

4.6 Isotherm Study

Adsorption isotherm is useful in investigating the feasibility of an adsorbent for an adsorbate. Freundlich and Langmuir isotherms provided deep insight to the adsorption of fluoride on MIAA, AA and AC, refer Figures – 4.7 and 4.8.

4.7 Freundlich Isotherm

The Freundlich model fitted well for all the adsorbents with the regression coefficient R^2 of 0.98, 0.97 and 0.98 for MIAA, activated charcoal and activated alumina respectively. K_f is the Freundlich constant representing the adsorption affinity of the adsorbent towards the adsorbate molecules, and n represents the heterogeneity of the adsorbent. K_f value in case of MIAA is almost three times higher compared to the value for activated charcoal and almost two times higher than activated alumina. The value of n for all the adsorbents is greater than unity indicating that the amount adsorbed increases less rapidly than the concentration (Deng *et al.*, 2006). The nonlinearity of the adsorption isotherms proved because $n > 1$ as shown in Figure 4.7(a, b and c).

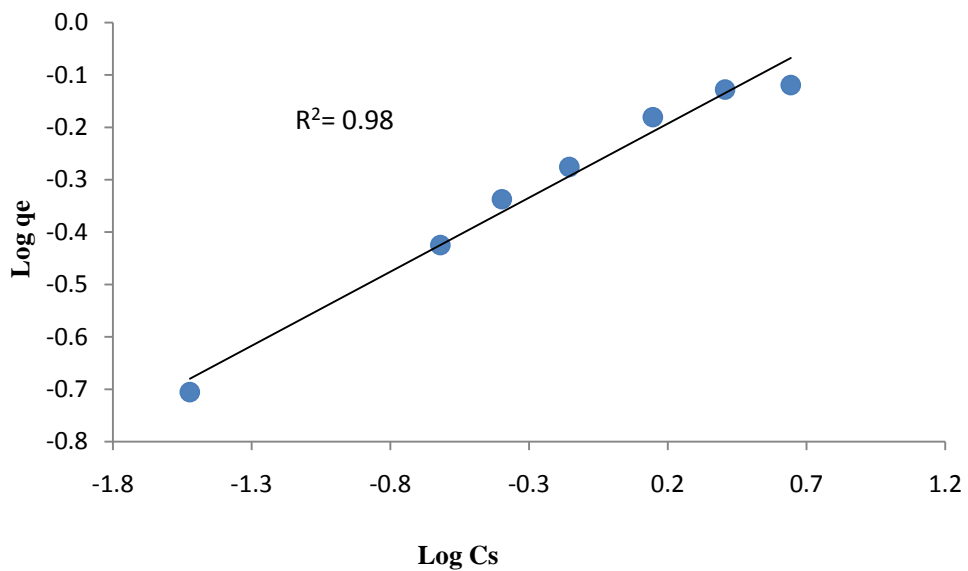


Figure 4.7(a): Freundlich isotherm for MIAA at $(20 \pm 1)^\circ\text{C}$

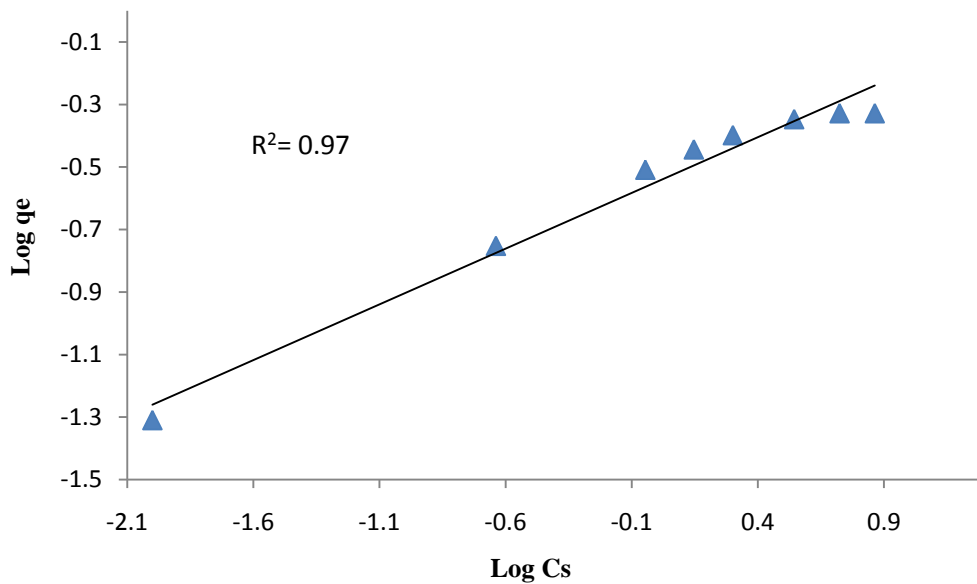


Figure 4.7(b): Freundlich isotherm for AC at $(20 \pm 1)^\circ\text{C}$

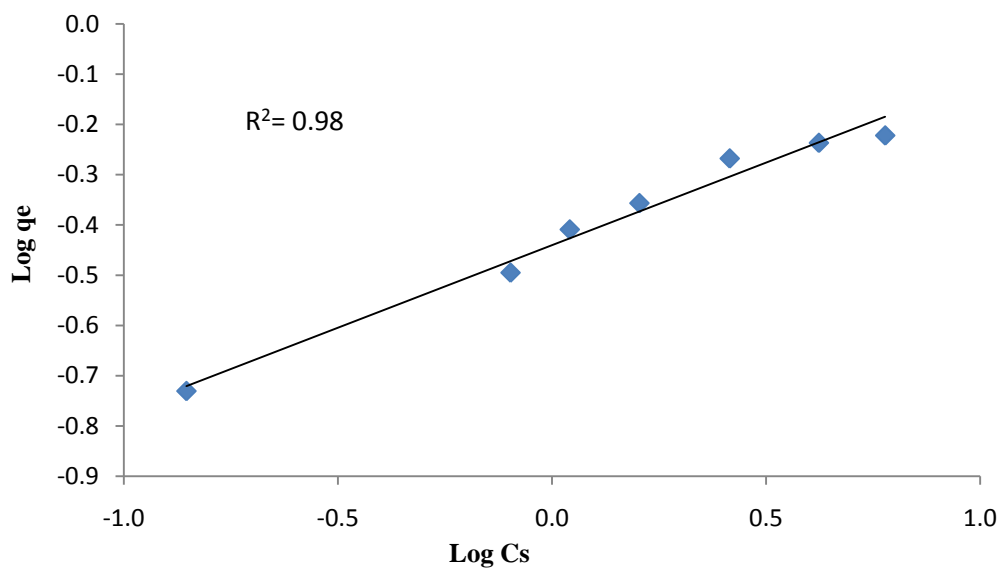


Fig 4.7(c): Freundlich isotherm for AA at (20±1 °C)

Table 4.3: Values of constants of Freundlich isotherm for MIAA, AC and AA

Adsorbent	Freundlich Constants	
	K_f	n
MIAA	0.60	3.57
AC	0.26	2.81
AA	0.35	3.04

4.8 Langmuir Isotherm

The Langmuir adsorption isotherm fitted very well for the fluoride adsorption on three adsorbents with the regression coefficient R^2 of 0.99 for MIAA and AC and 0.98 for AA as shown in Figure 4.8 (a, b and c). The values of the adsorption coefficient K and the monolayer capacity V_m calculated from Langmuir equation are given in Table-4.4. The values of K and V_m are higher for MIAA as compared to values for AC and AA that shows adsorption of fluoride on MIAA is more favorable.

The isotherm shape can be used to check whether an adsorption system is favorable or unfavorable. For this purpose Alagumuthu *et al.*, 2011 used the features of Langmuir isotherm that can be defined as equilibrium parameter or dimensionless separation factor R_L , defined by the following equation.

$$R_L = \frac{1}{1+KC_i} \dots\dots\dots (4. 1)$$

Where,

R_L = dimensionless separation factor

C_i = initial fluoride concentration

K = Langmuir constant

In this work, the R_L values calculated in the studied range of fluoride concentration ($C_i = 2 - 12$ mg/L) are determined to be in the range of 0.02–0.11 for MIAA, 0.03-0.16 for AC and 0.04-0.19 for AA which suggests favorable adsorption

of fluoride onto the MIAA, AC and AA at (20 ± 1 °C). It means Langmuir isotherm is favorable for three adsorbents in this study.

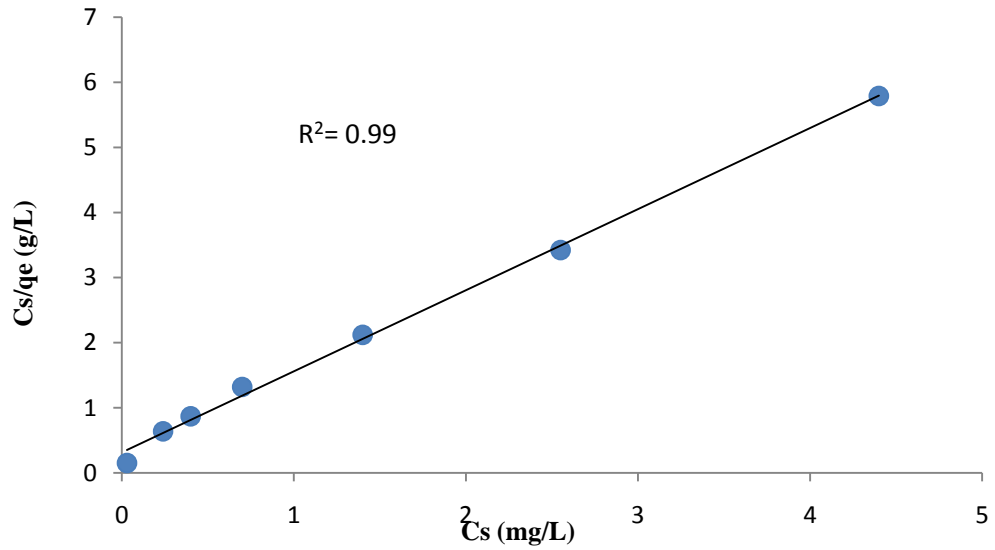


Figure 4.8(a): Langmuir isotherm for MIAA at (20 ± 1 °C)

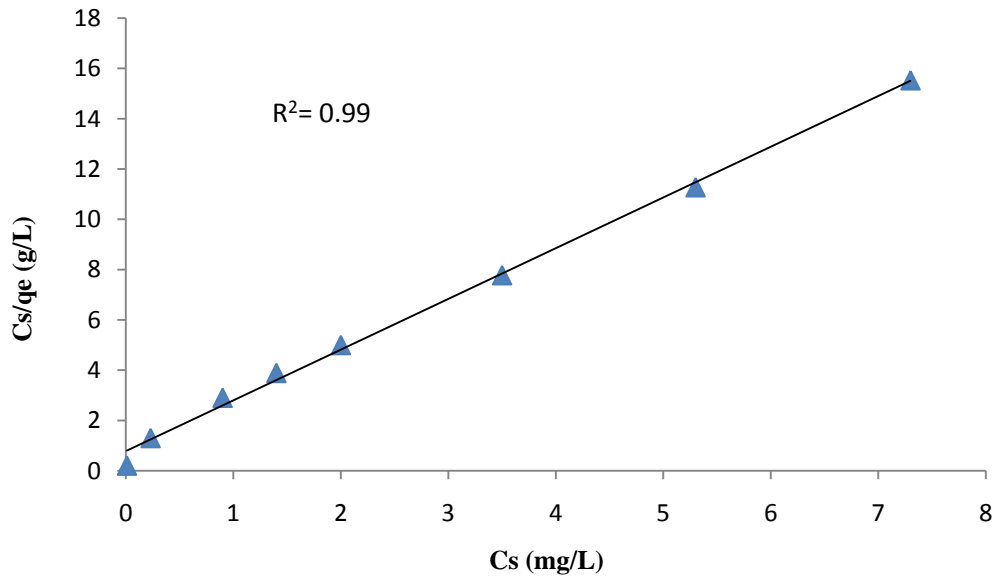


Figure 4.8(b): Langmuir isotherm for AC at (20 ± 1 °C)

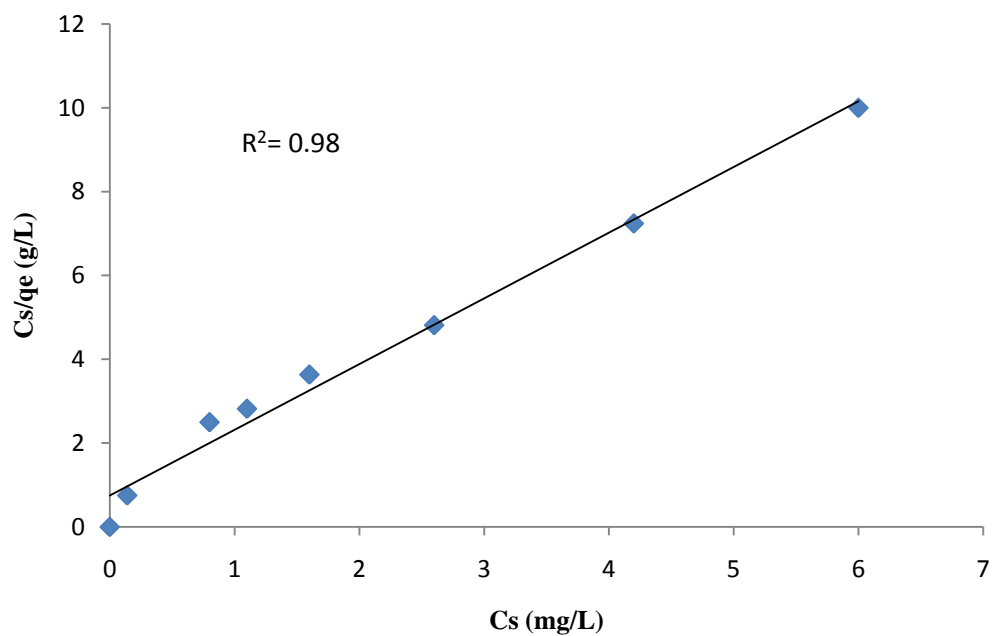


Figure 4.8(c): Langmuir isotherm for AA at (20±1 °C)

Table 4.4: Values of constants of Langmuir isotherm for MIAA, AC and AA

Adsorbent	Langmuir Constants	
	K	Vm
MIAA	4.03	0.80
AC	2.63	0.49
AA	2.08	0.64

Table 4.5: The value of R_L factor and type of isotherm

R_L	Type of isotherm
Greater than 1	Unfavorable
1	Linear
Between 0 and 1	Favorable
0	Irreversible

Table 4.6: The value of R_L at different initial fluoride concentration

C_i (mg/L)	R_L		
	MIAA	AC	AA
2	0.11	0.16	0.19
4	0.06	0.09	0.11
5	0.05	0.07	0.09
6	0.04	0.06	0.07
8	0.03	0.05	0.06
10	0.02	0.04	0.05
12	0.02	0.03	0.04

4.9 Regeneration Study

The results of regeneration showed in Figure 4.9. In case of thermal regeneration the removal efficiency of MIAA is up to 85% even after 5th sorption-desorption cycle. This might be due to the diffusion of fluoride ions into inner pores and the upper surface was again activated as the temperature for regeneration was same as for activation during calcination. But with chemical regeneration the efficiency was considerably decrease after every successive cycle. It may be because of vigorous washing after soaking in NaOH in order to neutralize the pH. However a detailed study is needed to investigate the reusability of MIAA.

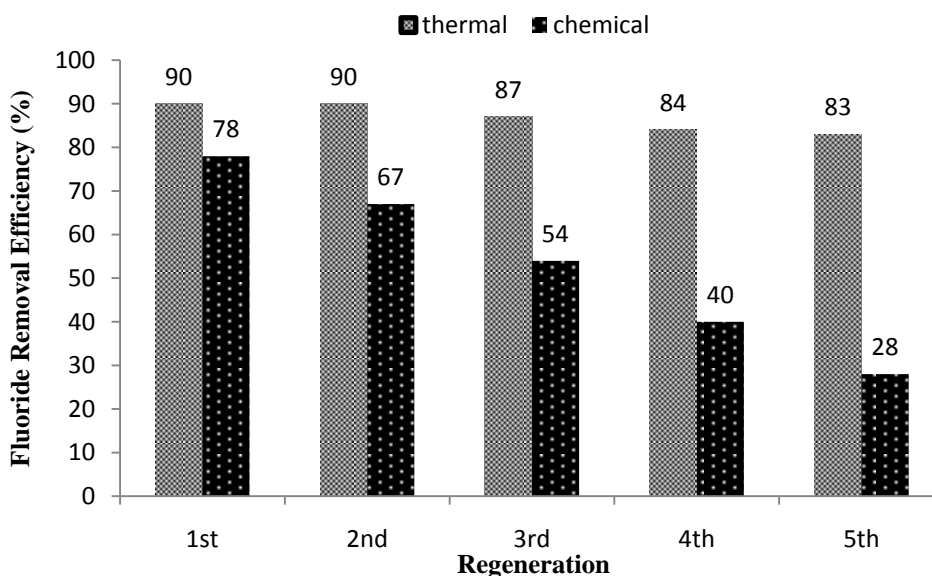


Figure 4.9: Regeneration of MIAA by thermal and chemical treatment

4.10 Real Water Sample Study

The MIAA was employed on real water samples in order to check its efficiency. The results of real water sample study were shown in Figure 4.10. In case of real water samples the removal efficiency was up to 75%. The decrease in the removal efficiency was due to the presence of other competing ions in real water samples. The sampling was done in fluoride endemic area of Pakistan that is Manga Mandi. Many fertilizers and aluminum industries are present in the surrounding of the area. The unchecked release of waste from the industries has led to the accumulation of considerable amount of fluoride into the resources such as water and soil.

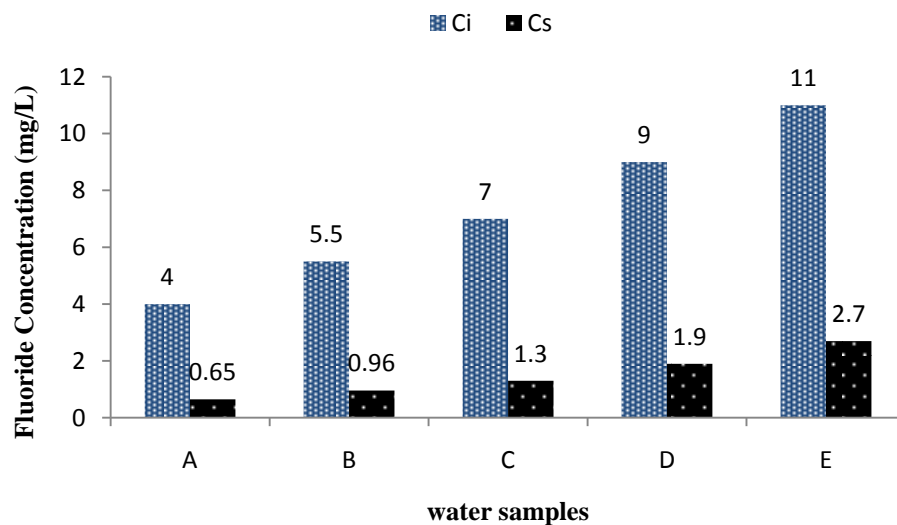


Figure 4.10: Real water samples with initial fluoride concentration (C_i) and final concentration (C_s)

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the present investigation the following conclusions may be drawn:

- i. Immobilization of modified activated alumina in the form of granules was achieved.
- ii. Maximum adsorption capacity of MIAA is 0.76mg/g at initial fluoride concentration of 12 mg/L and adsorbent dose of 10g/L, within the contact time of 60 minutes and stirring rate of 150rpm at 20±1°C.
- iii. At initial fluoride concentration of 12mg/L the maximum adsorption capacity of activated charcoal is 0.47mg/g at adsorbent dose of 10 g/L, while the contact time is 90 minutes and stirring rate is 100rpm at 20±1°C. While activated alumina attains maximum adsorption capacity within 60 minutes at 100rpm with 10g/L of the adsorbent dose at 20±1 °C.
- iv. The fluoride removal capacity of three adsorbents was in following order:
MIAA > AA > AC
- v. MIAA can be regenerated both chemically and thermally. But thermal regeneration gave more fruitful results than chemical regeneration.

- vi. MIAA proved effective for the treatment of fluoride contaminated actual drinking water samples.

5.2 Recommendations

As the new adsorbent has significant removal efficiency of fluoride. So there is need of further study therefore, following future studies are recommended:

- Further research work is required to investigate the effect of other parameters like pH, temperature and competing ions.
- The physicochemical properties of MIAA are required to investigate.
- Experimental design is required to develop the continuous treatment setup for drinking water purification refers Figure -5.1.

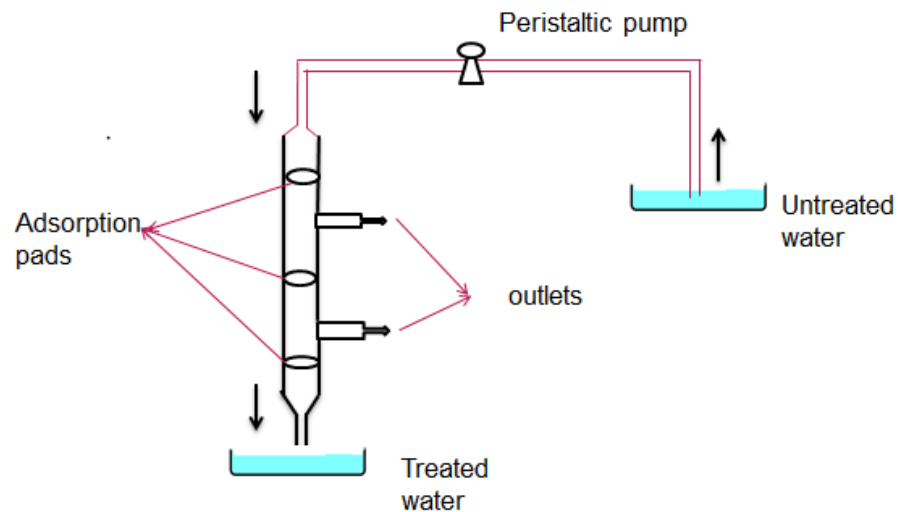


Figure 5.1: Proposed continuous water treatment setup

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APPENDIX - A
ADSORPTION STUDY OF MIAA

Adsorption study of MIAA

1.1 Dose

C_i (mg/L)	C_s (mg/L)				$x=C_i-C_s$ (mg/L)	m (g/L)	% Removal
	batch 1	batch 2	batch 3	avg.			
5	3.1	3.1	3.1	3.1	1.9	0.5	38
5	2.7	2.6	2.7	2.7	2.3	1	47
5	2	2.3	2.3	2.2	2.8	2	56
5	1.6	1.8	1.9	1.8	3.2	3	65
5	1.4	1.4	1.4	1.4	3.6	5	72
5	0.7	0.9	0.6	0.7	4.3	7	85
5	0.4	0.2	0.2	0.3	4.7	10	95
5	0.2	0.3	0	0.2	4.8	12	97
5	0	0	0	0	5	15	100
5	0	0	0	0	5	17	100
5	0	0	0	0	5	20	100

1.2. Contact Time

C_i (mg/L)	C_s (mg/L)				$x=C_i-C_s$ (mg/L)	m (g/L)	Time (min)	q_e (mg/g)
	batch 1	batch 2	batch 3	avg.				
5	4	4	4	4	1	10	5	0.10
5	3	3.1	3.1	3.1	1.9	10	15	0.19
5	2	2	2	2	3	10	30	0.30
5	1	0.9	0.9	0.9	4.1	10	45	0.41
5	0.3	0.3	0.3	0.3	4.9	10	60	0.49
5	0	0	0	0	5	10	75	0.50
5	0	0	0	0	5	10	90	0.50

1.3. Stirring Rate

C_i (mg/L)	C_s (mg/L)				$x=C_i-C_s$ (mg/L)	m (g/L)	Stirring Rate(rpm)	q_e (mg/g)
	batch 1	batch 2	batch 3	avg				
5	4.8	4.8	4.8	4.8	0.2	10	25	0.02
5	4.0	3.9	4.2	4.0	1.0	10	50	0.10
5	3.2	3.1	3.3	3.2	1.8	10	75	0.18
5	1.5	2.0	2.2	1.9	3.1	10	100	0.31
5	0.8	0.8	0.8	0.8	4.2	10	125	0.42
5	0.1	0.3	0.3	0.2	4.8	10	150	0.48
5	0.3	0.2	0.1	0.2	4.8	10	175	0.48
5	0.1	0.1	0.2	0.1	4.9	10	200	0.49

1.4 Initial Fluoride Concentration, Freundlich and Langmuir isotherm

C_i (mg/L)	C_s (mg/L)	$x=diff.$ (mg/L)	$m=dose$ g/L	q_e mg/g	C_s/q_e (g/L)	Log C_s	Log q_e
0.5	0	0.5	10	0.05	0	-	-1.30
2	0.03	1.97	10	0.20	0.15	-1.52	-0.71
4	0.24	3.76	10	0.38	0.64	-0.62	-0.42
5	0.4	4.6	10	0.46	0.87	-0.40	-0.34
6	0.7	5.3	10	0.53	1.32	-0.15	-0.28
8	1.4	6.6	10	0.66	2.12	0.15	-0.18
10	2.5	7.45	10	0.75	3.42	0.41	-0.13
12	4.4	7.6	10	0.76	5.79	0.64	-0.12

APPEDIX - B

ADSORPTION STUDY OF ACTIVATED CHARCOAL

2. Activated Charcoal

2.1 Dose

C_i (mg/L)	C_s (mg/L)				x= Diff (mg/L)	m= Dose (g/L)	% Removal
	batch 1	batch 2	batch 3	Avg			
5	3.5	3.5	3.5	3.5	1.5	0.5	30
5	3.1	3.2	3.0	3.1	1.9	1	38
5	2.3	2.3	2.3	2.3	2.7	2	54
5	1.8	1.8	1.7	1.8	3.2	5	65
5	1.3	1.2	1.1	1.2	3.8	7	76
5	0.9	0.7	0.7	0.8	4.2	10	85
5	0.7	0.7	0.7	0.7	4.3	12	86
5	0.6	0.6	0.6	0.6	4.4	15	88
5	0.6	0.6	0.6	0.6	4.4	17	88
5	0.6	0.6	0.6	0.6	4.4	20	89

2.2 Contact Time

Time (min)	C_i (mg/L)	C_s (mg/L)				x=diff. (mg/L)	m=dose g/L	q_e mg/g
		batch 1	batch 2	batch 3	Avg			
15	5	3.5	3.5	3.5	3.3	1.7	10	0.17
30	5	2.5	2.6	2.4	2.5	2.5	10	0.25
45	5	1.7	1.8	1.9	1.8	3.2	10	0.32
60	5	1.21	1.2	1.2	1.2	3.8	10	0.38
75	5	0.9	0.9	0.9	1.0	4.0	10	0.40
90	5	0.68	0.65	0.68	0.9	4.1	10	0.41
105	5	0.68	0.68	0.68	0.8	4.2	10	0.42
120	5	0.66	0.68	0.65	0.7	4.3	10	0.43

2.3 Stirring Rate

stirring rate	C_i (mg/L)	C_s (mg/L)				x=diff. (mg/L)	m=dose g/L	q_e mg/g
		batch 1	batch 2	batch 3	Avg			
25	5	3	3	3	3.5	1.5	10	0.15
50	5	2.2	2.3	2.3	2.8	2.2	10	0.2
75	5	1.5	1.6	1.6	1.8	3.2	10	0.3
100	5	0.7	0.6	0.6	1.0	4.2	10	0.4
125	5	0.6	0.6	0.6	0.6	4.4	10	0.4
150	5	0.5	0.5	0.5	0.6	4.4	10	0.4

2.4 Initial Fluoride Concentration, Freundlich and Langmuir isotherm

C_i (mg/L)	C_s (mg/L)	x=diff.(mg/L)	m=dose g/L	q_e mg/g	C_s/q_e (g/L)	Log C_s	Log q_e
0.5	0.01	0.49	10	0.05	0.2	-2.00	-1.31
2	0.23	1.77	10	0.18	1.3	-0.64	-0.75
4	0.9	3.1	10	0.31	2.9	-0.05	-0.51
5	1.4	3.6	10	0.36	3.9	0.15	-0.44
6	2.0	4.0	10	0.40	5.0	0.30	-0.40
8	3.5	4.5	10	0.45	7.8	0.54	-0.35
10	5.3	4.7	10	0.47	11.3	0.72	-0.33
12	7.3	4.7	10	0.47	15.5	0.86	-0.33

APPENDIX - C

ADSORPTION STUDY OF ACTIVATED ALUMINA

3. Activated Alumina

3.1 Dose

C _i (mg/L)	C _s (mg/L)				x= Diff (mg/L)	m= Dose (g/L)	% Removal
	batch 1	batch 2	batch 3	Avg			
5	3	3.8	3.5	3.4	1.6	0.5	31
5	2.5	2.9	2	2.5	2.5	1	51
5	1.7	1.7	1.7	1.7	3.3	2.5	66
5	1.3	1.0	1.0	1.1	3.9	5.0	78
5	0.6	0.8	0.5	0.6	4.4	7.5	87
5	0.5	0.6	0.4	0.5	4.5	10	90
5	0.4	0.2	0.4	0.3	4.7	12.5	93
5	0.1	0.3	0.5	0.3	4.7	15	94
5	0.3	0.3	0.3	0.3	4.7	17.5	94

3.2 Contact Time

Time (min)	C _i (mg/L)	C _s (mg/L)				x=diff.(mg/L)	m=dose g/L	q _e mg/g
		batch 1	batch 2	batch 3	Avg			
5	5	2.8	3.1	3	3.0	2.0	10	0.20
15	5	2.1	2.4	2.4	2.3	2.7	10	0.27
30	5	1.2	1.5	1.5	1.4	3.6	10	0.36
45	5	1	0.7	0.6	0.8	4.2	10	0.42
60	5	0.4	0.5	0.4	0.4	4.6	10	0.46
75	5	0.4	0.6	0.2	0.4	4.6	10	0.46
90	5	0.5	0.4	0.35	0.4	4.6	10	0.46

3.3 Stirring Rate

stirring rate (rpm)	C_i (mg/L)	C_s (mg/L)				$x=\text{diff.}(\text{mg/L})$	$m=\text{dose g/L}$	q_e mg/g
		batch 1	batch 2	batch 3	Avg			
25	5	3	3.1	2.7	2.9	2.1	10	0.21
50	5	2.1	2	1.6	1.9	3.1	10	0.31
75	5	1	1.3	1	1.1	3.9	10	0.39
100	5	0.6	0.2	0.5	0.4	4.6	10	0.46
125	5	0.2	0.2	0.3	0.2	4.8	10	0.48
150	5	0.1	0.3	0.3	0.2	4.8	10	0.48
200	5	0.2	0.1	0.4	0.2	4.8	10	0.48

3.4 Initial Fluoride Concentration, Freundlich and Langmuir isotherm

C_i (mg/L)	C_s (mg/L)	$x=\text{diff.}(\text{mg/L})$	$m=\text{dose g/L}$	q_e mg/g	C_s/q_e	$\text{Log } C_s$	$\text{Log } q_e$
0.5	0	0.5	10	0.05	0	-	-1.30
2	0.14	1.86	10	0.19	0.75	-0.85	-0.73
4	0.8	3.2	10	0.32	2.50	-0.10	-0.49
5	1.1	3.9	10	0.39	2.82	0.04	-0.41
6	1.6	4.4	10	0.44	3.64	0.20	-0.36
8	2.6	5.4	10	0.54	4.81	0.41	-0.27
10	4.2	5.8	10	0.58	7.24	0.62	-0.24
12	6	6	10	0.6	10.00	0.78	-0.22