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FLUORIDE REMOVAL USING MODIFIED SPENT DIATOMACEOUS EARTH ADSORBENTS

BY

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Fluoride Removal using Modified Spent Diatomaceous Earth Adsorbents

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This is to certify that the thesis prepared by TemesgenWolde entitled: **Fluoride removal using modified spent diatomaceous earth adsorbents** *and* submitted in partial fulfillment of the requirements for the degree of master of sciences (Chemical and Bio Engineering) complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, herebysubmitted by me, is my original work and has not previously been submitted for degreeat this or any other university, that all resources of materials used for this thesis havebeen duly acknowledged.

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LIST OF ACRONYMS AND ABBREVIATIONS

UNICEF	United Nation International Children Emergency Fund
USEPA	United State Environmental Protection Agency
CPHEEO	Central Public Health and Environmental Engineering
WHO	World Health Organization
MOWR	Ministry of Water Resource
ATDE	Acid Treated Diatomaceous Earth
ATSDE	Acid Treated Spent Diatomaceous Earth
ISE	Ion Selective Electrode
TISAB	Total Ionic Strength Adjustment Buffer
EDTA	Ethylene Diamine Tetra Acetic acid
MoWE	Ethiopian Ministry of Water and Energy
PZC-	Point of Zero Charge
BIS	Bureau of Indian Standards

ABSTRACT

Elevated concentrations of fluoride in drinking water are a serious health concern. Dental and skeletal fluorosis being the most commonly reported fluoride-related diseases in Ethiopian rift valley. Various naturally occurring materials have been explored as adsorbents for the removal of fluoride from water .This study investigate the fluoride removal capacity of spent diatomaceous earth from aqueous solution. The spent diatomaceous earth was collected, washed and dried in an oven at 110 ^{0}C for 24 hrs. The dried 10 gram of spent diatomaceous earth was reacted in 100 ml of 0.1M HCl and dried in an oven at 110 ^{0}C .The dried spent diatomaceous are powdered, sieved and preserved. The effect of processing conditions (pH, initial fluoride concentration, adsorbent dose and contact time) was investigated using batch adsorption experiments. The adsorption efficiency was increased with increasing contact time and adsorbent dose and decreased with increasing pH and initial fluoride concentration. At low pH (2) maximum amount of fluoride was adsorbed by acid treated spent diatomaceous earth (58.48).

Response surface methodology (RSM) involving Box–Behnken design was used to optimize the adsorption process of fluoride ions. The second order mathematical model was developed by regression analysis of the experimental data obtained from 29 batch runs. The optimum pH, initial fluoride concentration, adsorbent dose and contact time were found by desirability function to be 2.02,24.04mg/l, 18.83g and 2.95 hr respectively. Fluoride removal was 43.19% at the optimum combination of process parameters. The results of validation experiments conducted at optimum conditions for the removal of fluoride ions (42.94%) indicate that the predicted values are in good agreement with the experimental result. The adsorption data were well fitted to the Langmuir and Freundlich isotherm model. The adsorption capacity was 0.321 mg/g. Acid treated spent diatomaceous earth could be used as adsorbent for fluoride ion containing aqueous solution

1. INTRODUCTION

1.1. Fluoride in Natural Water

Occurrence of Fluoride

Fluorine is the most reactive and the most electronegative non–metal and therefore almost never occurs in nature in its elemental state. It is the 13th most abundant element in the earth's crust. It occurs in a combined form as fluorides in rocks and soil in a wide variety of minerals such as fluorspar (fluorite) (CaF_2), cryolite (Na_3AlF_6), apatite ($Ca_5(PO4)_3F$), and topaz $Al_2SiO_4(F,OH)_2$

Traces of fluoride are present in many natural waters, and higher concentrations often associated with ground waters. The release of fluoride to groundwater is dependent on chemical and physical processes that take place between the groundwater and its geological environment. Fluorite (CaF_2) is the predominant mineral that controls the dissolved fluoride concentration in the groundwater. Thus fluoride–rich ground waters are often associated with low calcium concentrations associated with rocks with low calcium content, or high pH conditions where sodium bicarbonate dominates the groundwater composition and calcium precipitates as calcite (CaCO3). Apart from the groundwater chemistry, hydrological properties (e.g., residence time) as well as climatic conditions (e.g., evapotranspiration, precipitation) and soil conditions (e.g., pH, soil type) have an influence on fluoride concentration

Drinking water is often the main source of fluoride intake by humans, especially in areas where fluoride concentrations in groundwater and/or surface water are high .In some areas, foodstuffs and/or indoor air pollution due to the burning of coal may make significant contributions to the daily intake of fluoride .On a local scale anthropogenic activities, such as the application of phosphate–containing fertilizers or aluminum smelting, may introduce considerable amounts of fluoride into the environment[1]

Global distribution of fluoride

High fluoride concentration in groundwater has been reported worldwide. Countries with significant groundwater fluoride contamination include India, Pakistan, China, Southern Africa, Iraq, Iran, Sudan, Uganda, Kenya, Ethiopia and Argentina [2] The Ethiopian Central Rift Valley is part of a large basin that extends from Syria and Jordan to Malawi and Mozambique. Due to its geological and climatic characteristics, it has some of world's highest concentrations of fluoride, mainly in deep wells in the semi-arid parts [3]

Of the total 1438 water samples tested in Ethiopia, 24.2% had fluoride concentrations above the 1.5 mg/L. Regionally; by far the highest fluoride levels were recorded in the Ethiopian Rift Valley, where 41.2% of all samples exceeded the 1.5 mg/L level. The highest fluoride concentrations were recorded in Ethiopian Rift Valley lakes Shale (264.0 mg/L) and Abijata (202.4 mg/L) and the lowest in Lake Tana (1.0 mg/L), and rivers, wells and springs in the highlands [4].

Health effects of fluoride

A higher daily dose has been linked to permanent dental and skeletal fluorosis It is estimated that more than 200 million people worldwide [5] rely on drinking water with fluoride concentrations that exceed the present WHO guideline of 1.5 mg/ L [6].According to estimates of the Ethiopian Ministry of Water Resources, more than 14 million people in the Ethiopian Rift Valley rely on drinking water contaminated by fluoride [7]

Dental fluorosis is characterized by chalky white, black areas on the tooth surface and mottled. Skeletal fluorosis affects children as well as adults. Fluoride mainly gets deposited in the joints of neck, knee, pelvic and shoulder bones and makes it difficult to move or walk. [8]

1.1.1. Guidelines for fluoride in drinking water

Taking health effects into consideration, the WHO has set a guideline value of 1.5 mg/L as the maximum permissible level of fluoride in drinking waters. However, it is important to consider climatic conditions, volume of water intake, diet and other factors in setting national standards for fluoride. As the fluoride intake determines health effects, standards are bound to be different for countries with temperate climates and for tropical countries, where significantly more water is consumed. Although water is generally the major route of fluoride intake, exposure from diet and air may become important in some situations.[9]

Table 1 Drinking water standards for fluoride prescribed by various organizations [10]

No.	Organizations	Permissible limit of Fluoride concentration (mg/L)
1	WHO	1.5
2	US Public Health Standard	0.7-1.2
3	BIS (IS 10500)	1.0-1.5
4	Indian Council of Medical Research	1.0-2.0
5	CPHEEO	1.0-1.5

1.1.2. Fluorosis mitigation options

Search for alternative sources
If the fluoride concentration in a community's water supply is significantly and consistently beyond the permissible level, it is essential to consider remedial measures to combat fluorosis.
a) Search for water with a lower fluoride level
b) Provision of a new and alternate source of water with acceptable fluoride levels
c) Blending high fluoride with low fluoride water
d)Dual water sources
e) Rainwater harvesting [10]

1.1.3. Technologies for fluoride removal from water

Defluoridation, a water treatment process, reduces the fluoride level to the permissible concentration for drinking water Defluoridation technologies can be broadly divided into four categories based on the fluoride removal mechanism. These include precipitation, membrane separation, ion–exchange, and adsorption methods [11]
Coagulation precipitation, also called the Nalgonda technique, is one of the popular techniques widely used for defluoridation of water in developing countries (e.g. India, Kenya, Senegal and Tanzania). Lime and alum are the most commonly used coagulants .Addition of lime leads to precipitation of fluoride as an insoluble fluorite. As lime leaves a residue of8.0mg/L, it is used in conjunction with alum treatment to ensure proper fluoride removal. Coagulation methods are generally found to be effective in defluoridation, but they are unsuccessful in decreasing fluoride to desire concentration levels. In addition, the method suffers drawbacks such as the formation of toxic soluble aluminum complexes, an increase of pH and total dissolved solids of the treated water, so the process needs a supplementary reaction for eliminating the excess chemicals. [12]
Membrane processes such as reverse osmosis (RO), nano–filtration (NF), and electro dialysis have also been used for fluoride removal from water .RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semi–permeable membrane. RO membrane rejects ions based on size and electrical charge. Reverse osmosis produces water of extremely high purity. Ndiayeet al, studied fluoride removal from effluents using RO technique. It was observed that the rejection of fluoride ion was typically higher than 98%,. Nano–filtration makes use of the same overall phenomenon as reverse osmosis except that the membranes have slightly larger pores than those used for reverse osmosis and

Reverse osmosis systems result in significant water loss and are not suitable for arid regions where water scarcity is a serious problem.

Electrodialysis (ED) is a membrane process similar to RO, except that it uses an applied dc (direct current) to separate ionic contaminants from water. ED process is energy–intensive

Ion–exchange resins have also been evaluated for fluoride removal from drinking water. Fluoride can be removed from water with a strongly basic anion–exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction:

$\text{Matrix–NR}_3^+\text{Cl}^- + \text{F}^- \rightarrow \text{Matrix–NR}_3^+\text{F}^- + \text{Cl}^-$

The fluoride ions replace the chloride ions of the resin.[11]

Adsorption process

Adsorption process is a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds. Adsorption is considered as an effective technology for fluoride removal because of its easy operation and relatively low cost. The adsorption process involves three steps:

1) Diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution

2) Adsorption of fluoride ions on to particle surfaces;

3) The adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials. [13]

1.1.4. Adsorbents used for defluoridation

The efficiency of the adsorption technique mainly depends on the nature of the adsorbents, so new, easy available and high loading capacity adsorbents having a strong affinity for fluoride ions are needed. Various naturally occurring materials available abundantly free of charge have been explored as adsorbents for the removal of fluoride from water. Recent attention of scientists has been devoted to the study of low cost, but effective materials. A large number of materials have been tested, such as clay, activated alumina, alumina-gibbsite. Activated carbon, calcite, zeolite, bleaching earth, red mud, brick powder [40] and diatomaceous earth [18]

1.1.5. Diatomaceous Earth

Diatomaceous earth or kieselguhr, also known as Diatomite, is a fine sedimentary rock of biogenetic origin, which mainly consists of amorphous hydrate and silica of diatomite resembles Opal or hydrous silica in composition (SiO_2-nH_2O). It is usually derived from the skeletons of aquatic plants called diatoms, but it is partly composed of alumina. The bulk of the chemical composition of diatomite (usually 70−90%), is silica and the remains include alumina (0.6−8%), iron oxide (0.2−3.5%), alkali metal oxides, Na_2O and MgO(less than 1%), CaO (0.3−3%) and a minor amount of other impurities, such as P_2O_5, and TiO_2.Sometimes, the deposits of the diatoms are only consisting of shell, but it may be contain other sediments such as clay and fine sand .Organic and inorganic materials, carbonates and metals oxides are the typical contaminants. [14, 15]

Diatomite has unique physical characteristics, such as high permeability, porosity small particle size, low thermal conductivity and density and high surface area. The properties of diatomite's surface, such as hydrophobia, solubility, charge, acidity, ion exchange and adsorption capabilities, are highly governed by the presence of water, which is partially structurally connected to the crystal mesh of the diatomite, forming active hydroxyl groups on it [14]

Diatomite is used to filter drinking water, sugar, honey, and syrups without altering of their natural properties. Diatomite has been already used for the removal of fluoride from aqueous solution either natural or modified form (chemically or thermally).Results of studies have shown that modified diatomite holds potential to adsorb fluoride. Acid treated diatomaceous earth [16] and thermal treated diatomaceous earth [17] and also diatomaceous earth [18]

1.2. Statement of the problem

In the Ethiopian Rift Valley (ERV) many sources of drinking water are contaminated with naturally-occurring fluoride. Of the total 1438 water samples tested in Ethiopia, 24.2% had fluoride concentrations above the 1.5 mg/l [4]. It is estimated that up to 14 million people in the ERV depend on fluoride-contaminated water for drinking. Elevated concentrations of fluoride in drinking water are a serious health concern, with dental and skeletal fluorosis being the most commonly reported fluoride-related diseases. So far deflouridation methods used, such as adsorption by activated alumina and bone chare, reverse osmosis, Nalgona technique and contact precipitation. However, these methods suffer from drawback such as high cost, rejection for cultural and religious reasons, maintenance difficulties and secondary pollution.[7] Hence, there is a need to find locally–available defluoridation media.

Diatomite is widely used in filtering processes. It is used to filter simple syrup in Pepsi production. The waste diatomaceous earth (spent diatomaceous earth) is dumping. So, the rationale of this research work was to investigate the capacity of spent diatomaceous earth for fluoride removal from aqueous solution and modification to enhance adsorption capacity and so which could be a good source of low cost adsorbent and reduce environment pollution as result of dumping.

1.3. Significance of study

Due to the substantial amounts of spent diatomaceous earth discarded in the field or simply disposed of as landfill and this investigation looks at the potential of spent diatomaceous earth as an adsorbent material for fluoride. The development of a suitable application of spent diatomaceous earth will not only minimize the potential environmental risks that environment pose but it will also reduce cost adsorbent and costs associated with the landfill

1.4. Objectives

1.4.1. General objective

The main objectives of this work were to examine the feasibility of using spent and acid treated spent diatomaceous earth as an adsorbent for the removal of fluoride from aqueous solution

1.4.2. Specific objectives

- Investigation of spent and acid treated diatomaceous earth on fluoride remove capacity from aqueous solution
- Determination of the composition of acid treated spent diatomaceous earth
- Determination of point of zero charge of acid treated spent diatomaceous earth
- To investigate the effect of processing conditions(pH, adsorbent dose ,contact time and initial fluoride concentration) on the fluoride removal capacity of acid treated spent diatomaceous earth using batch adsorption experiments
- To investigate the effect of co–existing anions on fluoride adsorption onto acid treated spent diatomaceous earth

1.5. Scope of the Study

The scope of this study was investigating the capacity of spent diatomaceous earth for fluoride removal from aqueous solution. Though there were several methods have been suggested in literature to improve the properties of clay materials. Which improve specific surface area, pore volume, acidity, activated sites and adsorption capacity. Among methods, chemical modification was selected for the study which uses hydrochloric acid. The study covers characterization and batch adsorption processes parameters

2. LITERATURE REVIEW

2.1. Adsorbents for defluoridation of water

2.1.1. Natural materials as adsorbent

Various naturally occurring materials available abundantly free of charge have been explored as adsorbents for the removal of fluoride from water .Wambuet al. used acid treated diatomaceous earth (ATDE) for fluoride removal. The equilibrium was attained in 10 min. The fluoride removal was increased from 40% to 92% when the solution temperature was raised from 293 to 303K. The adsorption process was slightly affected by pH change and dropped the fluoride removal from 98.8 to 98% when the pH of solution rose from 1.59 to 6.89. The presence of chloride ions slightly affected the adsorption whereas sulphate, nitrate and phosphate ions did not affect the fluoride removal from water. Complete fluoride removal could be achieved at 400 mg/l initial fluoride concentration at 0.5 g/ml dose, 303-313 K temperature and pH = 3.4±0.2. The Langmuir maximum adsorption capacity of ATDC was 51.1 mg/g. The adsorption process was impulsive and endothermic in nature [16]

Janta et al. investigated the ability of thermally treated and raw diatomaceous earth .Influential parameters such as contact time, pH and adsorption isotherm were also studied. The results showed that the diatomite heated to 500 ºC performed better than other heat treatment products and the equilibration time needed for fluoride removal by the adsorbents was reached within 60 min. The removal of fluoride was maximum at pH 2. The capacity of the adsorbents for removing fluoride is independent of the pH when the pH is higher than 4. The best fitting adsorption isotherms for the raw and calcinated diatomite are the Langmuir model with the maximum adsorption capacities of 2.253 and 4.162 mg/g, respectively [17]

Izuagieet al. studied the defluoridation of groundwater by using diatomaceous earth (DE). The maximum adsorption capacity and removal of fluoride for 8 mg/l of spiked water were 0.6525 mg/g and 25.62% at optimum conditions (pH of 2.0., an adsorbent dosage of 8 g/l, contact time of 30 minutes, temperature of 298K and shaking speed of 200 rpm). The presence of phosphate ions greatly reduced the fluoride adsorption capacity at low pH. The adsorption process obeyed Freundlich isotherm and pseudo-second-order kinetic model. The leaching of metal and non-metal species from diatomaceous earth was negligible. [18]

Fluoride removal by montmorillonite clay has also been evaluated by Karthikeyan et al. Fluoride uptake was found maximum at pH 2, and it decreased with increase in pH. Montmorillonite clay is made up of metal oxides which hydrolysed in aqueous solution. The decrease in the adsorption of fluoride on its surface reflects a reduction in quantity of the positive charges. The point of zero charge (pzc) of Montmorillonite is 2.5. The Langmuir maximum sorption capacity for fluoride was found to be 1.485–1.910 mg/g at different temperatures. Fluoride removal was found to be adversely affected only in the presence of HCO_3^-.Adsorption occurred on the surface as well as through intraparticle diffusion pattern of the adsorbent material. X-ray diffraction studies confirmed the deposition of fluoride on the surface of the clay material. FTIR studies also showed the involvement of hydroxyl group present on the surface in the adsorption interaction. [19]

Fluoride adsorption characteristics of clays collected from different areas in Ethiopia were assessed by Tikariha and Sahu. They also reported that the composition of clay mainly consist the metal oxides of Fe and Al were found to have the better potential as sorbents for fluoride from aqueous solutions. Three different types of clay Bombawoha, Kombolcha and Mugher were found to have the better potential as fluoride adsorbents. The effect of contact time, amount of adsorbent dose, pH, particle size, and heat treatment of adsorbent was investigated. The adsorption was rapid during the first one hour. The adsorption efficiency of fluoride increased with adsorbent dosage. The defluoridation capacity was appreciable within acidic range. Clay adsorbents, heat treated between 400 to 600 °C, gave better fluoride removal. The pH of the solution was found to be the most important factor affecting adsorption potential. Results also revealed that better adsorption was achieved in the acidic range, up to 3 to 6 with maximum adsorption potential at pH 3. Heat treatment at temperatures of up to 600 °C was observed to increase adsorption. [20]

Kim et al. used pyrophyllite clay for defluoridation of water. This clay mainly consists of Si (74.03%) and Al (21.20%). The maximum adsorbent capacity of pyrophyllite clay was 0.737 mg/g with particle size less than 0.15mm. The equilibrium condition occurred in around 24 hours. The adsorption reaction was endothermic in nature. The fluoride was not sensitive to the pH range of 4 to 6. The effect of sulfate, carbonate and phosphate co-anions were important whereas effect of nitrate and chloride ions were negligible. The clay calcined at 400^0C gave 21% higher fluoride removal capacity as compared to un-calcined ones [21].

Mogesetal, Used fired clay chips as an alternative water defluoridating media. The maximum amount of fluoride removed after equilibration was about 90% and 80% for solutions kept at pH 3 and 9, respectively. The maximum adsorption capacity of the adsorbent for defluoridating 1-2 litres of water was found to be 0.2 mg/g by the adsorbent dose of 30g. The structure of the clay plays a very important role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. In general, the more positive the surface the better the sorption will be for negatively charged ions, such as fluoride [22]. In general, it was observed by Agarwalet al and Zhuang and Yu that firing and chemical pretreatment both improve the adsorptioncapacity of some clays and soils [23.24]

Zevenbergenetalstudied the defluoridation of water using the Ando soil of Kenya and defluoridation capacity is 5.5mg/g at PH 4.5. It was concluded that the use of Ando soils appears to be an economical and efficient method for defluoridation of drinking water [25]

Bjorvatn.et al. studied the defluoridation of water using soil samples from Ethiopia. It was reported that the soil samples from highland areas around Addis Ababa reduced the fluoride content of the water from 15 to 1mg/L with dose of about 100g/l [26]

Coetzee et al .investigated the defluoridation capacity of South African clay for natural water various clay types such as bauxite, laterite, bentonite and kaolinite were tested for fluoride adsorption. Clays consisting of substantial amounts of gibbsite or aluminum oxides exhibited best overall potential as fluoride adsorbents. The optimum pH was 5.0 and 3.5 for aluminum oxide and iron oxide type adsorbents pH adjustment and activation of clay substrates were found to improve the adsorption capacities of some clay. [27]

Gomoroetal .investigated the ability of thermally treated laterite soils to remove fluoride from water. XRD and XRF spectroscopic analysis of the soil samples were done to show defluoridating capacity. Important issues considered in this study including the relation between the mineral composition of soils, their ability to remove fluoride and the effect of thermal treatment of the soil. Study of kinetics of fluoride removal by the adsorbents indicated that fluoride removal by the soil samples involves two mechanisms with different rate constants: an initial rapid adsorption of fluoride on the surface of the adsorbent followed by slower diffusion of the fluoride into the interior of the adsorbent. The maximum capacity was 0.893mg/g obtained at500 ºC. The results obtained indicate that there was strong correlation between fluoride removal capacity and gibbsite content of the soil. From this it can be concluded that gibbsite is the active component in lateritic soils that strongly influence the fluoride removal capability. Speciation analysis reveals that at low initial fluoride concentrations the dissolution of gibbsite was facilitated by the adsorption of fluoride onto gibbsite and this may result in the formation of aluminium-fluoro complexes in water. [28]

Sarkar et al used laterite for defluoriation from aqueous solution in batch mode. The mechanism of fluoride removal was governed by the zero point charge of laterite. The pH_{pzc} of laterite was reported 3.98 and was found to be responsible for fluoride adsorption. Lowering of pH enhanced fluoride removal from the solution. Fluoride adsorption decreased from 0.2014 to 0.1586 mg/g as the solution pH increased from 2.1 to 6.7, and decreased on further rise in pH above 7.5. The Langmuir sorption capacity of laterite for fluoride was 0.8461 mg/g at 303 K [29]

Meenakshiet al. used raw kaolinite (RK) and micronized kaolinite (MK) clay by mechano chemical activation for defluoridation of water. The optimum pH for maximum removal of fluoride was observed to be 3.0 and defluoridation capacity of RK and MK was 0.120 mg/g and 0.134 mg/g respectively. The equilibrium was reached within 30 minutes for both materials. The presence of co-anions affected the defluoridation capacity in the order of $F^->HCO_3^->Cl^-$, SO_4^{3-}, and NO_3^-. The experimental data of MK fitted well with Langmuir isotherm than Freundlich isotherm model. The Langmuir adsorption capacity of MK at 303K, 313K and 323K temperature was 0.609, 0.714 and 0.782 mg/g respectively. [30]

Karthikeyanet al. studied the defluoridation capability of two naturally occurring earth materials (EM) from aqueous solution. The effective fluoride removal was observed with the dose of adsorbent of 6g/50ml and 8g/50ml for EM1 and EM2 respectively. The removal of fluoride was not affected in the pH range of 3 to 9 but gets reduced at higher pH of 11.0. The experimental data fitted well with Freundlich isotherm. The Langmuir adsorption capacity of EM1 and EM2 was observed to be 0.067 and 0.058 mg/g respectively. The adsorption reaction was endothermic in nature. [31]

Ramdanietal .investigated the adsorption characteristics of Algerian clay types to assess their potential as adsorbents for simple defluoridation systems. One of the clay contained a higher percentage of calcium (AC) and the second one was without calcium (ANC). The adsorption increased up to pH 4 and decreased at higher pH. The Langmuir monolayer capacity for AC and ANC was found to be 1.013 and 1.324 mg/g. The adsorption mechanism was proposed to be an interaction between the metal oxides at the surface of the montmorillonite and fluoride ions. The chemical activation of clay was found effective in adsorption reaching up to 88% whereas the thermal activation was ineffective as adsorption reached only around 5% [29]

The removal of fluoride was also studied using acid activated kaolinite clay by Gogoi and Baruah .The activation of clay was performed with conc. H2SO4. The clay of 300 mesh size showed maximum adsorption of fluoride due to the availability of larger specific surface area on the adsorbent surface. The optimum pH for fluoride removal was pH 4. The Langmuir maximum sorption capacity of the acid activated clay for fluoride ranged between 0.0450 and 0.0557 mg/g at different temperatures. [32]

Modification of bentonite clay with aluminum in order to enhance its adsorption capacity for f fluoride ions from water was conducted by Vijai et al. The pH, contact time, adsorbent dose, temperature and adsorbent size were investigated. At low pH (pH=2) the maximum amount of fluoride is adsorbed by the Al -bent clay (51%). The amount of fluoride adsorbed almost constant in the removal of fluoride, when the dosage of the adsorbent is 8g and it has rapidly reached equilibrium at three hours and high percentage of fluoride was adsorbed. The amount of fluoride adsorption in the larger particles has less sorption than the smaller particles, because the larger particles have less surface area. Generally fluoride adsorption increased from 40% to 49% with the maximum temperature 70°C.Theresults indicated that the Al-bent clay can be successfully used as an effective adsorbent for fluoride removal. [33]

According to Gandhi et al., adsorption study of fluoride was done through batch process by using red soil. From this study it was found that percentage removal increased with contact time and adsorbent dosage and the optimum contact time for red soil was within 15 minutes. The percentage removal of fluoride decreased with increased in concentration. Langmuir and Freundlich adsorption isotherm model and pseudo-second- order kinetic were best fitted in this adsorption study. Here, the red soil as natural adsorbent was selected also to reduce the cost of the material and abundantly available. The red soil did not cause any increase in pH, or any increase of other ions in the effluent and drinking water. [20]

Vithanageet al. used laterite rich in iron (40%) and aluminum (30%) for defluoridation of water. The fluoride removal was maximum at pH<5.0. Fluoride adsorption followed the Freundlich isotherm. The surface complexation modeling showed that both Fe and Al sites of the laterite surface contributes to fluoride adsorption via inner-sphere complexation. The laterite-fluoride interaction was strong chemisorptions surface complexation [29]

Wambuet al. used acid treated lateritic mineral (LM-1) from Kenya for defluoridation of water in batch mode. The percentage of fluoride removal was increased with the presence of nitrate and chlorate ions whereas reduced in the presence of sulphates, chloride and phosphate ions. The optimum condition for maximum fluoride removal was observed at pH 1.59, a dose of 4g/20ml and 313K temperature. The experimental data fitted well with Freundlich isotherm than the Langmuir isotherm model. The Langmuir maximum adsorption capacity of the LM-1 adsorbent was 10.4792 mg/g at 303K.The ion-exchange mechanism of OH- with fluoride helped defluoridation. [34].

Wambuet al. used ferric poly-mineral (FPM) from Kenya for defluoridation of water in batch mode. The adsorption reaction was fast and about 90% removal was achieved within 30 min. with 1000mg/l of initial fluoride concentration at pH 3.32 and 293K and using 0.2 g/ml adsorbent dose. The fluoride uptake was decreased with higher concentration of co-anions and found in order of nitrate > phosphate > chloride >sulphate ions. The experimental data fitted well with the Langmuir isotherm model. The Langmuir maximum adsorption capacity of adsorbent was 12.7 mg//g at 323K. The fluoride adsorption onto FPM was a diversified process involving chemisorption surface site followed by gradual intra-particle penetration of F- into mesoporous structure of the mineral. [35]

Wambuet al. used siliceous mineral of a Kenyan origin (M1) for defluoridation of water in batch and column study. The initial batch equilibrium was attained within 20 min. The adsorption capacity was increased with an increase in temperature and decrease in pH of the solution. The fluoride removal close to 100% was obtained using initial fluoride concentration of 200 mg/l at 0.5 g/ml adsorbent dose, 303-333K temperature and pH 3.4±0.2. The experimental results fitted well with Langmuir isotherm. Langmuir adsorption capacity was found to be 12.4 mg/g. The co-anions effect on fluoride removal was in order of chloride > nitrate >sulphate. [36]

2.1.2. Industrial wastes as adsorbent

Widespread industrial activities generate huge amount of solid waste materials as by-products. One of the beneficial uses of these wastes is to convert them as inexpensive sorbents (wherever applicable) for the detoxification of water and wastewater. Various industrial wastes have been examined with or without treatment for fluoride removal from water.

Fly ash

The ability of fly ash (a thermal power plant waste) to remove fluoride from water and wastewaters was studied by Chaturvedi et al. The removal of fluoride was found favorable at low concentration, high temperature and acidic pH. The Langmuir maximum sorption capacity of fly ash for fluoride ranged from 20.0 to 20.3 mg/g. [37]

Alum Sludge

Alum sludge is one of the waste products generated during the manufacture of alum from bauxite by the sulphuric acid process and mainly consists of oxides of aluminum and titanium with small a mounts of silicates. Each of these oxides is known to possess adsorption and ion exchange properties. To take advantage of these properties of alum sludge, Sujana et al. examined its use as an adsorbent for the removal of fluoride from polluted waters. The data indicate that treated alum sludge surface sites were heterogeneous in nature and that fitted into a heterogeneous site binding model. The Langmuir maximum sorption capacity for fluoride removal by alum sludge was reported to be 5.394 mg/g. [38]

The industrial waste residue, generated during the manufacture of aluminum sulphate (alum) from kaolin by the sulphuric acid process was used as defluoridating media by Nigussie et al. The percentage of fluoride removal remained nearly constant within the pH range of 3–8. With further increase in the solution pH, the removal efficiency decreased and the declining trend became significant at pH values >10. The presence of positively charged and neutral sites at the surface of the adsorbent in the pH range up to 8 was mentioned as the reason for better fluoride removal in that range.. The adsorbent fluoride removal efficiency was affected significantly with bicarbonate ion concentrations and little or no effect by other anions such as phosphates, chlorides, sulphates and nitrates. [39]

Red mud

The removal of fluoride from aqueous solution using the original and HCl-activated red mud (an aluminum industry waste) has also been studied. The fluoride adsorption capacity of the activated form was found to be higher than that of the original form. The maximum removal of fluoride ion was obtained at pH 5.5. It was found that the required time for adsorption equilibrium of fluoride ions was 2 h. The removal of fluoride ion using red mud was explained on the basis of the chemical nature and specific interaction with metal oxide surfaces, and the results were interpreted in terms of pH variations. The Langmuir maximum sorption capacity of activated red mud for fluoride was calculated to be 6.29 mg/g. [38]

The capability of coal mining wastes for fluoride removal from aqueous solution was investigated by C inarli et al. The Langmuir maximum sorption capacity of the adsorbent for fluoride was reported 15.67 mg/g. The removal of fluoride was found favorable at low pH and the optimum pH for fluoride adsorption was found to be 3.5[38]

Spent bleaching earth (SBE)

Spent bleaching earth (SBE), a solid waste from edible oil processing industry, was treated with acid and used for fluoride adsorption from aqueous solution. The Langmuir maximum sorption capacity of treated SBE for fluoride removal was reported as 7.752 mg/g. Fluoride removal decreased with increasing pH and maximum fluoride removal was observed at pH 3.5.PO_4^{3-}, $SO4^{2-}$and NO_3^-adversely influenced the fluoride sorption capacity of acid treated SBE Furthermore, the equilibrium fluoride adsorption data for SBE were fitted by the Langmuir adsorption isotherm, indicating that fluoride uptake by acidified SBE surfaces was a chemisorption process [38]

Carbon slurry

Adsorption of fluoride on waste carbon slurry (a fertilizer industry waste) was investigated by Gupta et.al .The adsorption capacity of fluoride first increased up to pH 7.58 and then started to decrease till pH 9.68 and further showed a drastic decrease on further increasing the pH to 11.6. Maximum adsorption capacity (4.861 mg/g) of fluoride on carbon slurry was observed at 15 mg/L initial fluoride concentration using 1.0 g/L adsorbent dose. Langmuir maximum sorption capacity was reported as ca. 4.3–5.5 mg/g at different temperatures. [38]

Bottom ash

Adsorption of fluoride on bottom ash was investigated by Ramesh et al. In this study, adsorption potential of bottom ash was investigated for defluoridation of drinking water using batch and continuous fixed bed column studies. Batch adsorptive defluoridation conducted under experimental conditions such as pH, temperature, particle size, agitation time and dosage. The optimum pH was found to be pH 6 with the maximum efficiency of 83.2 %. Also the fluoride removal increased with a decrease in the particle size. The optimum contact time for fluoride was found to be 105 minutes with the maximum efficiency of 73.5 % at 70 mg/100 ml bottomash dosage. Adsorption isotherms had been modeled by Langmuir and Freundlich isotherms. The maximum monolayer adsorption capacity of bottom ash was found tobe16.26 mg/g at 303 K.[20]

2.1.3. Zeolite

Zeolite has large surface area and having ability to exchange weakly bond cations with those in solution and hence attracted many research to adopt as adsorbent for water and wastewater treatment. Onyango et al. investigated the fluoride sorption characteristics of zeolite F-9 containing surface-active sites created by exchanging Na^+-bound zeolite with Al^{3+} or La^{3+} as they show good affinity for fluoride. It was concluded by the authors that the uptake of fluoride by Al3$^+$ - exchanged zeolite proceeded by an ion-exchange mechanism, while fluoride-La^{3+} –exchanged zeolite interaction proceeded by physical adsorption. Fluoride removal from water was affected by the solution pH and bicarbonate content. Bicarbonate buffered the system pH to higher values and thus diminished the affinity of the active sites for fluoride sorption. The

Langmuir maximum equilibrium sorption was found to be 2.04–4.13 mg/g for various metal loaded zeolites. [40]

Sun et al. used $FeCl_3$ modified natural stilbite (Fe(III)-STI) zeolite for defluoridation of water in batch study. The removal efficiency of 92% was achieved with 10 mg/l of initial fluoride concentration at equilibrium time of 2h, pH of 6.94 and dose of 10g/l. The experimental information fitted well with Langmuir isotherm model. The Langmuir maximum adsorption capacity was 2.31 mg/g [40]

2.1.4. Alumina and aluminium-based adsorbents

Activated alumina

Activated alumina has been an adsorbent of interest and studied for years for fluoride removal from drinking water. Farrah et al. studied the fluoride ion interaction with amorphous Al(OH)3, gibbsite or alumina (Al_2O_3) over a wide pH range (3–8) and F^- concentrations (1.9–19gm/l). It was found that at pH < 6 and total F:Al ratios >2.5, most of the amorphous $AI(OH)_3$ gel dissolved through the formation of AlF complexes, with the distribution of fluoride ions being determined by the equilibrium F^-value. At lower F:Al ratios, some solid persisted in the pH 4–7 region and strongly sorbed F^- from solution. Authors observed maximum uptake of F^-in the pH range of 5.5–6.5 (up to 171 mg/g). At lower pH, fluoride uptake decreased due to the preferential formation of AlFx soluble species; at higher pH, OH^- displaced F^- from the solid and the amount of F− sorbed or converted to complexes declined rapidly towards zero between pH 6 and 8. At a fixed pH (between 5 and 7.5), fluoride uptake varied in accordance with Langmuir model (maximum capacity ∼19mg/g). The amount of substrate converted into AlFx complexes in acid media increased with decreasing pH and increasing initial fluoride concentration. Gibbsite displayed the same dissolution trends, but reacted at a much slower rate. Less F− was sorbed by this substrate (0.19–0.38 mg/g). [41]

Ghorai and Pant investigated the removal of fluoride using activated alumina (AA) (Grade OA-25) in batch and continuous operations. An adsorption capacity of 1.450 mg/g was obtained at pH 7. Percentage fluoride removal increased in the pH range from 4 to 7 and decreased thereafter. Silicates and hydroxyl ions were considered to compete more strongly with F− ions for alumina exchange sites at pH > 7, whereas, at pH < 7, the soluble alumino-fluoro complexes were formed resulting in the presence of aluminum ions in the treated water. Early saturation and lower fluoride removal was observed at higher flow rate and at higher concentration. There was a marginal decrease in the uptake capacity after each regeneration cycle. [41]

Pietrelli also investigated the potential of metallurgical grade alumina (MGA) for the adsorption of fluoride under different experimental conditions. The maximum adsorption rate occurred at pH 5–6, the fluoride ions are under F^- ionic forms which confer a maximum stability to the fluoro-alumina interaction. The fluoride adsorption onto MGA sites decreased drastically at higher pH values, which was attributed to the competition with hydroxide ions for the binding on the MGA surface. Langmuir maximum adsorption capacity of MGA for fluoride was found to be 12.57 mg/g. [41].

Shimelis et al. have compared the adsorption capacities of untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminum sulphate for fluoride removal from aqueous solution. The removal efficiency of fluoride increased with increase in adsorbent dosage. Fluoride adsorption efficiencies showed an increase with rise in the thermal treatment temperature up to 200 ˚C, but further increase in temperature resulted in lower removal efficiency. In continuous packed bed column, treatment at 300 ◦C was taken as an optimum value. High defluoridation efficiency was achieved using both UHA and THA within a pH range of 4.0–9.0. The adsorption data fitted well to the Freundlich isotherm model with a minimum capacity of 23.7 mg F^-/g and 7.0 mg F^-/g for THA and UHA, respectively [42]

Modified activated alumina

To enhance the adsorption efficacy of activated alumina, researchers have also modified alumina surface.

Alumina plus manganese dioxide

Maliyekkal et al. also modified alumina with manganese oxide to prepare manganese-oxide-coated alumina (MOCA) and investigated the potential of sorbent for defluoridation of drinking water by batch and continuous mode experiments. Adsorption of fluoride on to MOCA was found to be much faster than that of AA at the initial period of time and was almost constant after 3 h. The limited extent of adsorption after 3 h was attributed to the surface treatment of AA which had shifted pHzpc to a lower level. Optimum removal of fluoride ions occurred in a pH range of 4–7. The Langmuir maximum sorption capacity of MOCA for fluoride was about 2.65 times higher than that of AA (2.851 mg/g). The MOCA was effectively regenerated using 2.5% NaOH

Teng et al. prepared a novel hydrous-manganese-oxide-coated alumina (HMOCA) by coating hydrous manganese oxide onto alumina surface through a redox process and used it for defluoridation. The manganese oxides were amorphous and manganese existed mainly in +IV oxidation state. The prepared adsorbent could reduce fluoride concentration from 6.0 to 0.45 mg/L at an initial pH of 5.2 ± 0.05, while the removal efficiency was 45% for the virgin activated alumina under the same condition. The optimum initial pH range of fluoride adsorption by HMOCA was 4.0–6.0 with removal efficiency higher than 95%. The removal efficiency dramatically decreased and the adsorbent exhibited negligible adsorption (6.3%) at pH 11.1. Fluoride removal mechanism by HMOCA was explained by anion exchange between hydroxyl ion and fluoride in the acidic pH range. The increased pH after adsorption was attributed to the liberation of hydroxyl ions. At pH > 6.0, fluoride was thought to be absorbed by van der Waals forces. The surface of HMOCA was considered electronegative when the initial pH was above 6.0 since the pHpzc of HMOCA was found to be 5.9, which would prevent the movement of F^{-}towards HMOCA surface due to the Coulombic repulsion. The reason for the decrease in adsorption in alkaline solution was explained by the strong competition between hydroxide ions and fluoride on active adsorption sites. The presence of HCO_3^{-}, $SO_4^{2-}$and PO_4^{3-}showed negative influence on the adsorption of fluoride. The adsorbed fluoride was released by alkali solution.[40].

Alumina plus magnesium oxide

Maliyekkal et al. developed a magnesia–amended activated alumina (MAAA) prepared by impregnating alumina with magnesium hydroxide and calcining the product at 450 ºC. MAAA adsorbed fluoride from drinking water more effectively than activated alumina. More than 95% removal of fluoride (10 mg/L) was achieved with in 3 hr of contact time at neutral pH, bringing concentration down to only 0.5 mg/L. Adsorption of fluoride on to MAAA was found to be pH–dependent and a decrease in sorption was observed at higher pH. An optimum fluoride removal was observed in the pH range of 5.0–7.5. The maximum adsorption capacity for fluoride was 10.12 mg/g in the fluoride concentrations range from 5 to 150 mg/L. Most of the co–existing ions found in the natural water source studied had negligible effect on fluoride sorption by MAAA. However, higher concentrations of bicarbonate and sulfate reduced the fluoride adsorption capacity. The fluoride bearing MAAA was regenerated with 2% sodium hydroxide solution [40]

Alumina plus iron oxide

Biswaset al. studied the adsorption capacity of iron (III) – aluminium (III) mixed oxides made by co-precipitated aluminum and iron hydroxides from a chloride mixture in equimolar quantities using ammonia, the resulting mixed hydroxide, after aging and drying, is a better adsorbent for fluoride than either aluminum hydroxide or iron (III) hydroxide.Fourier transform infrared (FTIR) spectra indicate the presence of the Fe–O–Al bond. Scanning electron microscopy (SEM) showed an almost irregular surface morphology with high porosity, indicative of a high surface area. The monolayer adsorption capacity of the mixed hydroxide, derived from Langmuir isotherms, was greater than for the pure hydroxides. [41]

Chubaret al. studied the anion adsorption capacity of an adsorbent precipitated from equimolaraluminum and iron (III) chloride by addition of ammonia. The anions investigated were fluoride, chloride, bromide and bromate. At pH 4, fluoride was the most strongly adsorbed at 88 mg F-/g of adsorbent [41]

Kamble et al.have reported the effectiveness of alkoxide origin alumina, γ_-alumina containing small amounts of Fe_2O_3 and SiO_2 as well as activated carbon in its pores, for defluoridation of drinking water. Alkoxide origin alumina sorbent showed lower equilibrium fluoride concentration as compared to the activated alumina. The maximum fluoride removal efficiency was observed in the pH range of 5–7. Carbonate, bicarbonate and sulphate reduced the fluoride sorption due to the change in solution pH and competition for active sorption sites. The reason for increased adsorption by the alkoxide origin alumina was attributed to the increased electropositivity and the small hydrophobicity retained on the alkoxide origin alumina. [41]

2.1.5. Iron-based adsorbents

Iron-based materials have also been extensively studied for fluoride removal as iron shows better affinity towards fluoride. Most of the adsorbents for fluoride removal have been tested for drinking water, and would not be stable at extreme pH values unless the pH is adjusted. Thus, polishing industrial wastewaters containing excess fluoride stands as a major problem

Streat et al performed adsorption experiments by batch and mini-column scale to test the potential of granular ferric hydroxide (GFH) for the removal of various ions including fluoride. Adsorption of fluoride onto GFH was found to be strongly pH dependent. With the increase in pH, the fluoride capacity decreased. [43]

Granular ferric hydroxidewas also used for defluoridation of water by Kumar etal.under various operational parameters. An adsorption capacityof 7.0 mg/g was observed for fluoride on GFH at pH 6.0–7.0at room temperature (25°C). Fluoride adsorption was found todecrease particularly sharply above pH 8, as the surface chargebecomes more negative (pHzpc of GFH is. 8). The fluoride adsorptiononto GFH was attributed to the interaction of fluoride withsingly coordinated

FeOH surface groups and the mechanism of fluorideadsorption was described as an exchange reaction against OH− of surface groups. The OH/F exchange has also found to suggest that the fluoride ion can be considered as fully located in the surface. The inner-spherically sorbing anions such as phosphate and sulphate significantly influenced the sorption of fluoride at the elevated concentrations where the sorption competition occurred for the limited amount of sorption sites on GFH. Another form of an iron bearing oxide mineral i.e. goethite (FeOOH), has wide scale application as an adsorbent due to its character of adsorption of various important oxyanions and cations in its complex matrix. [44]

Liu et al. have also conducted fluoride removal using synthetic siderite which has been found to be a potential sorbent for the adsorption of arsenic. The synthetic siderite showed high adsorption capacity for F^-removal, which was up to 1.775 mg/g in the batch experiments with an adsorbent dosage of 5 g/L and an initial F^-concentration of 20 mg/L at 25 ^{0}c. The presence of Cl^- andNO_3^- had less effect on F^-adsorption, while PO_4^{3-}significantly affected F^- removal from aqueous solution. The authors explained the mechanism of fluoride removal by synthetic siderite with the help of SEM and XRD results. The high removal efficiency of synthetic siderite was attributed to the adsorption of fluoride on the fresh goethite with large specific surface area. Co-precipitation of ferric hydroxide with fluoride, which was caused by dissolution of pristine synthetic siderite and subsequent oxidization of Fe^{2+},was also found to contribute to the fixation of fluoride on the adsorbent [45].

2.1.6. Calcium-based adsorbents

Extensive research has also been carried out for the removal of fluoride using various calcium salts as calcium has a good affinity for fluoride anion. Turner et al. conducted fluoride removal studies using crushed limestone (99% pure calcite) by batch studies and surface-sensitive techniques from solutions with high fluoride concentrations ranging from 3 to ∼2100 mg/L. With the help of surface-sensitive techniques, such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as potential measurements, the authors were able to confirm that a combination of surface adsorption and precipitation reactions removed fluoride from aqueous systems; the degree of removal being dependent on calcite surface area. The results proved that fluoride adsorption occurred immediately over the entire calcite surface with fluorite precipitating at step edges and kinks, where dissolved Ca^{2+} concentration was highest AFM and potential measurements confirmed that adsorption was instantaneous because surface morphology was immediately affected. Dissolution increased Ca_{2+} concentration in solution, saturation with respect to CaF_2 was reached and fluorite precipitated where local concentration gradients were highest, at the edges of retreating terraces. Dissolution continued, despite adsorbed F− and precipitating fluorite, replenishing dissolved Ca^{2+}, allowing further precipitation of CaF_2, and the cycle continued. Fluorite continued to precipitate until calcite could dissolve and supply $Ca^{2+.}$[46]

Activated and ordinary quick lime was also evaluated for their performance as adsorbents for fluoride removal from aqueous solutions. The removal of fluoride was 80.6% at optimum conditions from the synthetic solution when initial fluoride concentration was 50 mg/L. The Langmuir maximum sorption capacity of activated quick lime for fluoride was 16.67 mg/g. Scanning electron microscopy (SEM) micrographs and X-ray diffraction (XRD) studies revealed that the removal of fluoride was mainly due to chemisorption and precipitation. The anions reduced the fluoride adsorption in the order, $PO_4{}^{3-} > SO_4{}^{2-} > NO_3{}^{-}$. [47]

2.1.7. Nano–adsorbents

Nanotechnology has emerged as a promising technology in past decade in various fields. Likewise, use of nano–particles as adsorbents for water treatment is also gaining wide attention in recent years. Carbon nano–tubes (CNTs) have attracted huge interest since their discovery. Their small sizes, large surface area, high mechanical strength and remarkable electrical conductivities make them potential materials for a wide range of promising applications.

Wang et al. performed defluoridation experiments employing nano-scale aluminium oxide hydroxide as sorbent, taking into account the advantage of higher surface area of nanoparticles as compared to the traditional micron-sized materials. The maximum Langmuir defluoridation capacity of nano-AlOOH was found to be 3.259 mg/g. The adsorption of fluoride onto nano-AlOOH was strongly pH dependent. The fluoride adsorption increased with the rise in pH, reaching a maximum of 96.7% at pH 6.8, and then decreased with further increase in pH. The pHpzc of the sorbent was 7.8, which was responsible for the sorption of fluoride at acidic pHs and low efficiency in alkaline medium was explained by the repulsion between the negatively charged surface and fluoride. The XPS analysis of the sorbent indicated that the adsorption of fluoride at low pH(pH <pHpzc) could be explained by a two-step protonation/ ligand exchange reaction mechanism and exhibited participation of surface OH group in fluoride removal. Adsorption of fluoride at initial pH > 7.8 was attributed to van der Waal forces and not by anion exchange, which was evident from the decrease in final pH. At pH > 7.8, nano-AlOOH was said to function as a cation exchange [40]

Taking into consideration the advantages of magnetic separation process and potential of activated alumina for defluoridation,Chang et al. synthesized two effective types of super paramagneticnano-scale adsorbents of bayerite/SiO_2/Fe_3O_4 via three sequential steps: chemical precipitation of Fe_3O_4, coating of SiO_2on Fe_3O_4 using acidifying method, and further coating of bayerite($Al(OH)_3$) on SiO2/Fe_3O_4 adopting sol–gel (MASG) or homogeneous precipitation (MAHP) methods for the elimination of fluoride from aqueous solution and compared the adsorption potential of the prepared sorbents with that of commercial activated alumina (CA).The Langmuir isotherm well described the equilibrium of fluoride adsorption on CA, MASG, and MAHP. The result revealed that the adsorption capacity of CA could effectively be enhanced when the initial pH value was 3.5, which was the approximate pK value of the dissociation constant of hydrofluoric acid. MASG was found to be the most effective adsorbent, of which the adsorption capacity was reported as 38 g/kg and it competed with CA even at a higher pH value such as 6.0 versus 3.5. The removal of fluoride ions in the solution with MASG and MAHP suspended was attributed to the functional [40]

2.1.8. Apatite and hydroxypatite adsorbent

Apatite in various forms has been used for fluoride removal shows good potential for defluoridation. In a study conducted byGao et al. synthetic nano-hydroxyapatite (n-HAp), biogenicapatite (bone meal; B), treated biogenic apatite (bone mealprepared by H2O2 oxidation, BH2O2) and geogenic apatite (rockphosphate) were employed to compare their efficiency for fluoride removal. The extent of fluoride removal was greatly increased to90.94% (2.27 mg/g) with 0.1 g/25 ml of n-HAp, 86.45% (2.18 mg/g) of B, and 88.01% (2.20 mg/g) of BH_2O_2. The results revealed that n-HAp showed the best adsorption capacities for fluoride removal as compared to the other apatites used in this study. BH_2O_2hadhigher fluoride adsorption capacity as compared to bone meal sorbent as the former consisted of more inorganic phase. Due to this low rate of release of OH−, rock phosphate exhibited very low fluoride removal efficiency. The maximum fluoride removal by n-Hap was 87.07% at pH 2.0 and a gradual decrease in fluoride adsorption was observed with increase in the pH. In case of adsorbents B and BH_2O_2 the fluoride removal first dramatically increased to78.95% and 84.35% at pH 5.06, and then slightly decreased to 61.12%and 72.84% at pH 11.0. Optimal adsorption was obtained in the wide initial pH range 5.0–6.0 for all the adsorbents studied. [48]

Mourabet et al., studied on the fluoride adsorption onto hydroxyapatite using response surface methodology (RSM). Hydroxyapatite had been characterized by using different physicochemical methods. In order to determine the effects of parameters namely temperature (20-40 °C), initial solution pH (4-11), adsorbent dose (0.1-0.3 g) and initial fluoride concentration (10-20 mg/ L) on fluoride uptake from aqueous solution, a three-level, four-factor, Box–Behnken design had been employed. The second order mathematical model was developed by regression analysis of the experimental data obtained from 29 batch runs. The optimum pH, temperature, adsorbent dose and initial concentration were found by desirability function to be4.16, 39.02 °C, 0.28 g and 20 mg/L, respectively. Fluoride removal was 86.34 % at the optimum combination of process parameters. The time data fitted well to pseudo second order kinetic model. According to the correlation coefficients, the adsorption of fluoride on the hydroxyapatite was correlated well with the Langmuir and Freundlich models. [49]

Sundaramet al. synthesized n-HAp by precipitation method and employed the sorbent for fluoride removal. The authors conclude that fluoride removal decreased with increasing pH and the maximum defluoridation capacity was reported as 1845 mg F^-/kg at PH 3 and only 570 mg F^-/kg was removed at pH 11. The variation in fluoride removal capacity at different pH was attributed to the protonation of the adsorbent surface at acidic pH and formation of negatively charged surface in alkaline pH. The pH_{zpc} of n-Hap was found to be 7.88.Fluoride removal mechanism was governed by both ion-exchange and adsorption process. There was no significant influence of other co-anions like chloride, nitrate and sulphate on the DC of n-HAp except bicarbonate ions [50]

2.1.9. Building materials as adsorbent

Togarepi et al showed in their study that heat and chemically treated sand was applied as an adsorbent for the removal of fluoride ions from aqueous solutions. The influence of different parameters such as calcinations time, dosage, initial fluoride concentration and pH were evaluated. Results indicated that activated sand can be used for defluoridation of water. This can be achieved by coating sand with 10 % Fe2O3, a calcination time of 3 hrs and pH around 6. The adsorption also increased with initial fluoride concentration and adsorbent dose. This study also showed that up to 90 % of fluoride was adsorbed with 12 g of adsorbent in 50 ml of 10 mg/L fluoride solution. The sorption data were best described by the Freundlich isotherm. The maximum adsorption capacity was found to be 10.3 mg/g. According to these findings, physico-chemically modified sand has potential application as an adsorbent for fluoride ions removal. The Langmuir and Freundlich isotherms were used to model the equilibrium sorption data. The results showed that using an optimum dose of 0.24 g/ml, up to 90 % fluoride removal could be achieved and the optimum pH was in the range 5.7 to 6.3. It was also shown that a calniation period of 3hrs using 10 % Fe_2O_3 for chemical treatment gave optimum results for fluoride removal [51]

Chen et al. used a new material, ceramic adsorbent to evaluate the feasibility for fluoride removal from aqueous environment. Batch experiments were performed to study the influence of various experimental parameters such as contact time (0-48 hrs), initial fluoride concentration (20-100 mg/L), pH (2-12) and the presence of competing anions on the adsorption of fluoride on ceramic adsorbent. The experimental data revealed that both the Langmuir and Freundlich isotherm models fitted well with the fluoride sorption process. The adsorption capacity of ceramic adsorbent for fluoride was 2.16 mg/g at 30 °C. The optimum fluoride removal was observed between pH ranges of 4.0-11.0 indicating the ceramic adsorbent has promising potential utility in practical application. The adsorption process was well decreased in the presence of phosphate followed by carbonate and sulphate. Results from this study demonstrated potential utility of ceramic adsorbent that could be developed into a viable technology for fluoride removal from aqueous environment. In this study, a novel sorbent, ferrous-amended ceramic adsorbent has been prepared and examined for its potential in removing fluoride from aqueous environment. It's explained with pseudo-second-order kinetic model. The fluoride adsorption was granular structure; high surface area and effective capacity of fluoride removal make the adsorbent a highly potential media to be used in purification of fluoride from water. The fluoride adsorption was reduced in the presence of carbonate, phosphate and sulphate and increased slightly in the presence of chloride and nitrate ions. The ceramic adsorbent also can be regenerated several times with 0.1M HCl as effluent. Therefore, the new ceramic adsorbent was a promising material for fluoride removal from water environment. [52]

Rani et al., used brick powder for defluoridation. Different parameters pH, effect of dose and contact time of adsorbed were studied and optimized. For the optimum condition i.e. pH (6-8) and dose of adsorbents (0.6-1.0 g/100ml), the percentage of defluoridation from aqueous (synthetic) sample, was found to be increased from 29.8 to 54.4 % for brick powder with the increase in contact time of 15 to 120 min. Fluoride removal was found to be48.73 and 56.4 % from groundwater samples having 3.14 and 1.21 mg/L fluoride, respectively under the optimized conditions. Defluoridation capacity of brick powder can be explained on the basis of the chemical interaction of fluoride with the metal oxides under suitable pH conditions. [20]

2.1.10. Carbon based adsorbent

According to Ibrahim and Khazaal, dynamic adsorption studies were performed to study the suitability of coal ash to remediate fluoride contaminated water. A series of experiments were conducted with aqueous solutions containing 2.5,5, 10, 50 and100 mg/L at 29 °C in a column packed with 500 g of coal ash. The flow rate through the bed was 2 ml/hrs. The effects of contact time, initial adsorbate concentration and sorbent particle size range on fluoride removal efficiency were studied. Better removal efficiencies were obtained with lower particle size ranges. The fluoride concentration in the effluent gradually decreased reaching 0 mg/L after96-168 hrs depending on the initial adsorbate concentration. The kinetic results showed that defluoridation followed first order kinetics. An empirical formula was proposed to describe the relationship between the fluoride removal efficiency and the dependent operating variables with 95 % confidence level. Based on these studies, it is concluded that coal ash can be fruitfully utilized for the removal of fluoride from its aqueous solutions. A double mechanism was likely to operate in the retention of fluoride by coal ash: chemical binding by calcium hydroxide and physical sorption by residual carbon particles. The percentage of fluoride removal was found to be a function of contact time and initial solute concentration. The removal increased with time and with increasing initial solute concentration an equation for the estimation of the value of reaction rate constant as a function of the initial fluoride concentration was proposed. The developed empirical formula, for the removal efficiency represented the present experimental data with 95 % confidence level with a correlation coefficient of 0.9698[20]

Low-cost pine wood and pine bark chars, obtained as a byproduct from fast pyrolysis in an auger reactor at 400 and 450 °C, were characterized and used as received for water defluoridation. Adsorption studies were performed at different temperatures, pH values, and solid to liquid ratios in the batch mode. Maximum fluoride adsorption occurred at pH 2.0. A kinetic study yielded an optimum equilibrium time of 48 hrs with an adsorbent dose of 10 g/L. Sorption isotherm studies were conducted over a concentration range of 1-100 mg/L. A kinetic study yielded an optimum equilibrium time of 48 hrs with an adsorbent dose of 10 g/L. Sorption isotherm studies were conducted over a concentration range of 1-100 mg/L. Fluoride adsorption decreased with an increase in temperature. The char performances were evaluated using the Freundlich, Langmuir [20]

Gupta et al. developed a micronanohierarchalweb (MiNaHiWe) consisting of activated carbon fibers (ACF) and carbon nano fibers (CNF), impregnated with Al for the removal of fluoride from wastewater. It was observed that pre-treatment of the feed water was not required while using the Al-CNF for treating the wastewater with pH 5.0–8.0.[53] Using a redox process, granular activated carbon (GAC) was coated with manganese oxides and the prepared sorbent (GAC-MnO_2) was used for fluoride removal from aqueous solution The adsorption capacities of the coated GAC obtained with a 0.3 M $MnCl_2$ exhibited maximum fluoride sorption capacity in comparison with other coated GAC, and at least three times greater than those of uncoated GAC. The pH of the solution influenced fluoride removal, and the optimum equilibrium pH for fluoride adsorption was observed to be 3.0. [54]

According to Dutta et al., adsorption of fluoride was done from its aqueous solution by using microwave assisted activated carbon. The activated carbon was prepared by carbonization of Acacia auriculiformisscrap wood char followed by microwave heating. A batch study on fluoride sorption was carried out at various experimental conditions including different pH, initial fluoride concentrations, adsorbent concentrations, competitive anion chloride and different temperatures .Fluoride adsorption was found to be pH dependent and the maximum removal of fluoride was obtained at pH of 4.4. On the other hand, the fluoride adsorption was reduced in the presence of chloride ions. The percentage removal of fluoride was found to be increased with increase in temperature and adsorbent dose and a maximum removal of 97.2 % was obtained with an adsorbent dose of 2 g/L. On the other hand, the adsorption of fluoride was also increased with decrease in particle size and the maximum removal occurred at a particle size of 58 µm. In order to investigate the mechanism of fluoride removal, various adsorption isotherms such as Langmuir and Freundlich were fitted at 293, 303, and 323 K. The experimental data revealed that the Langmuir isotherm gave more satisfactory fit for fluoride removal and the monolayer adsorption capacity according to Langmuir isotherm was found to be 19.92 mg/g. [20]

2.1.11. Low cost adsorbent

The potential of bleaching powder for the removal of excess fluoride from aqueous solution was evaluated by Kagneet al.as it could be used both as disinfectant and defluoridating agent. The fluoride removal by bleaching powder was found to occur by adsorption (i.e., chemisorptions) and slightly due to precipitationin the form of calcium fluoride, which was confirmed by SEM images. An adsorbent dose of 50 g/L was found optimum for fluoride removal from aqueous solution. Bleaching powder exhibited reasonably significant fluoride removal over a pH range of 6–10.Formation of weakly ionized hydrofluoric acid and formation of $Ca(OH)_2$ in acidic and alkaline medium lowered fluoride removal. The presence of SO_4^{2-}, NO_3^-, and Cl^-ions was found to affect the fluoride removal, indicating that these ions might compete with each other for the sorption of fluoride. The Langmuir maximum sorption capacity of bleaching powder for fluoride was reported to be 0.1308 mg/g. [20]

According to Malakootianetal. fluoride removal from synthetic water by pumice (volcanic stone comprised of irregular connected as well as separated cavities and often composed from high amount of silica compounds (69 %) than other minerals) was studied at batch experiments. The effects of pH, contact time, fluoride concentrations and adsorbent dose on the fluoride sequestration were investigated. Increasing of the absorbent amount, contact time and pH improved the efficiency of fluoride removal. The maximum fluoride removal of 85.75% was obtained in neutral pH, 180 minutes of contact time, 20 mg/l dose of pumice and 2 mg/l of initial fluoride concentration. The experimental results matched with Freundlich isotherm and pseudo-second-order kinetics. The maximum adsorption capacity and constant rate were found 0.31 mg/g and 0.21 mg/g.min respectively [55].

Sajiduetal.used raw bauxite for defluoridation of ground water and treated it in a model domestic defluoridation unit in batch mode. The optimum bauxite dosage and contact time were observed as 0.150 kg/L and 15.0 minute respectively. Sand and charcoal at a constant dose of 3:1 was used for water clarification and its optimum dose was 0.720 kg/L. The specific water yield by this defluoridation unit was found to be 36.0 L/kg adsorbent [29]

Buamah et al. used the high aluminum bauxite ore (HABO) of ground water. Within the pH range tested (5-7), the fluoride removal decreased with increasing pH. Occurrence of sulphate, chloride and nitrate in the model water reduced the fluoride removal capacity by 57, 24 and 38 % respectively. The combined effect of these anions showed a 60 % reduction in the fluoride removal capacity. TheFreundlich and Langmuir isotherms gave an adsorption capacity (K) of 0.90 mg/g forthe HABO. The adsorption kinetics fitted well the pseudo second-order kinetic model. The HABO is thermally stable and has kaolinite [$Al_2Si_2O_5(OH)_5$] and gibbsite[$Al(OH)_3$] as its major components.[29]

2.2. Factors affecting adsorption

Fluoride removal efficiency always depends on raw water quality profile, i.e., initial fluoride concentration, solution pH, environment temperature, contact time and adsorbent dose

The adsorption of fluoride ion by adsorbent depends on the interactions between the solution and the surface of adsorbent. Adsorption process can be assumed to be complete when equilibrium was achieved between the fluoride ions and the adsorbent. However, specific time was needed to maintain the equilibrium interactions to ensure that the adsorption process is complete

pH of the solution

Adsorption of fluoride ion from the wastewater is mainly influenced by the pH of the solution. pH can influence the surface charge of the adsorbent and the degree of ionization of the fluoride ions In a particular pH range, most fluoride ion adsorption was enhanced with pH, increasing to a certain value followed by a reduction when further pH increases. The dependence of the fluoride ion uptake on pH can be associated with both the surface functional groups on the adsorbent and also the chemistry of the solution [58]

Point of Zero Charge (PZC)

Solid metal oxides in contact with aqueous solutions typically become hydrated and form a monolayer of surface hydroxyl groups that may become protonated or deprotonated, depending on the $\mathrm{H^+}$ (aq) concentration. This amphoteric behavior allows the oxide particles to develop electrical charges that are either positive, when they receive protons (equation 1) or negative, when they release protons (equation 2).

$$\mathrm{M-OH(surf)+H^+(aq)=M-OH_2^+(surf)} \tag{1}$$

$$\mathrm{M-OH(surf)+OH^-(surf)=M-O^-(surf)+H_2O} \tag{2}$$

The resulting net charge Q, may be defined as the difference in concentration between the positive and negative sites per weight of the solid

$$\mathrm{Q=\{M-OH_2^+\,(surf)+M-O^-(surf)\}} \tag{3}$$

If the concentrations of the two types of sites resulting in equation 1 and 2 are the same, there will be no net charge on the surface. This condition is called the point of zero charge (PZC)

The point of zero charge can thus be measured by potentiometric titration if $\mathrm{H^+}$and $\mathrm{OH^-}$ are the only aqueous ions involved. In practice, however, electrolytes typically contain other anions,$A^-$and cations, $\mathrm{C^+}$ that may adsorb onto the surface sites as follows

$$\mathrm{M-OH_2^+}\,(surf)+\mathrm{A^-}=M-OH_2+\mathrm{A^-}\ \text{(surf)} \tag{4}$$

$$\mathrm{M-OH_2^+}\,(surf)+C^+=M-O^-\,C^+\,(surf)+2H^+(qa) \tag{5}$$

In these cases the net surface charge not only depends on the H^+ and OH^- ions in medium, but also on the concentration of the electrolyte [that provides A^-(qa), C^+(aq)]

A simple and fast method that gives a reasonable approximation to the PZC consists in locating the intersection of one or more titration curves performed with constant ionic strength and different amounts of solid, and that of a blank solution (i.e., without the solid). This is called the potentiometric mass titration method.[59].

Initial fluoride concentration

Initial concentration of fluoride ion can alter the fluoride removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind fluoride ions .Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of fluoride ion between the aqueous and solid phases. [58].

Temperature

Temperature plays a double role in the fluoride adsorption process. Temperature can impact the physical binding processes of fluoride to adsorbent. Most adsorption studies were conducted at room temperature in laboratory settings. As temperature increased, sorption was shown to be less favored most likely due to increased deprotonation or hydroxylation of the surface causing more negatively charges adsorbent surfaces This was an important observation to note when attempting to apply defluoridation methods on site in hot climates, for adsorption capacities attained under room temperature conditions may be higher than in the field as a result of increased temperatures [58]

3. MATERIALS AND METHODS

3.1 Materials and Apparatus

The types of laboratory materials and apparatus used were: nickel crucibles, analytical balance, spatula, pipettes, pipette filler, , oven, washing bottles, 50 mL plastic beakers, magnetic stirrer, magnetic rod, 50 mL graduated plastic tubes, filter funnels, filter papers, different sizes of volumetric flasks, beakers, pH/ISE meter (Orion Model, EA 940 Expandable Ion Analyzer)equipped with combination fluoride-selective electrode (Orion Model 96-09), pH/ion meter(WTW Ino lab pH/ION Level 2, Germany) using unfilled pH glass electrode are used

Chemicals

All solutions were prepared from analytical-reagent grade chemicals and distilled/deionized water. These includes glacial acetic acid (CH_3COOH), sodium chloride (NaCl), sodium citrate and EDTA, NaOH pellets, HC l(37% sp.gr. 1.19), buffer solutions for pH calibration, tri-sodium acetate, and sodium fluoride (NaF) are used

3.2. Methodology

3.2.1. Adsorbent collection and preparation

The adsorbent used in the study was spent diatomaceous earth, a waste generated from the production of soft drink beverage. The typical chemical compositions of diatomaceous earth from the manufacturer's EP Minerals Europe mainly consist of 89.0% SiO_2, 4.1% Al_2O_3, 1.5% Fe_2O_3, 0.3% MgO, 0.6 % Cao, other oxides 4 %, loss of ignition 1%. Spent diatomaceous earth was collected from summit soft drink beverage industry which is located around CMC in Ethiopia and washed with distilled water to remove fines and adhered impurity. Then spent diatomaceous earth was dried up in an oven at 110 ^{0}C overnight (24hours). Spent diatomaceous earth was removed from the oven and allowed to cool down. The dried spent diatomaceous earth was preserved in plastic container to protect from moisture and then standard sieves having a mesh size of 1.8 mm. A mass 10 gram each of spent diatomaceous earth was reacted into four 250 ml volumetric flasks containing 100mL of 0.1 M HCl solution. The flasks were magnetically stirred for time interval (30-210 min) to select best adsorbent from among the acid treated samples at different times. At the end of the stirred period, each of the samples was suction filtered and washed with excess distilled water to remove the ions and other residue and dried at 110 ^{0}C for 24 h and stored air tight glass bottle to protect it from moisture[16]

3.2.2. Characterization of the Adsorbent Materials

Determination of zero point charge

The point of zero charge (PZC) was measured by potentiometric mass titrations technique (PZC was identified as the common intersection point (CIP) of the potentiometric curve of the blank solution with the corresponding curves of the impregnating suspensions containing 0.5, 1.0, and 1.5 g of the adsorbent in electrolytic solution (0.02 N NaNO3 in 50 ml of deionized water). The experiment was performed, under an N2 atmosphere and the aqueous suspensions were equilibrated for 1 h to reach an equilibrium pH value. Small amount of 1 M NaOH was added to make the pH around 10 and recorded as initial pH after 15–20 min. Then the solid suspensions were titrated by 0.1 N HNO3, using 665 Dosimat (Metrohm, Switzerland). The pH of each suspension was then measured with 1 min time interval using a Switzerland). The pH of each suspension was then measured with 1 min time interval using a digital pH meter standardized by buffers (WTW InolabpH/ION Level 2, Germany). [60]

Analysis of chemical composition

The chemical composition of the acid treated diatomaceous earth sample was analyzed using $LiBo_2$ Fusion, HF attack, Gravimetric, Colorimetric and Atomic absorption spectroscopy

Fourier transforms infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of the adsorbent were recorded with Fourier transform infrared spectrophotometer in the range of 400-4,000 cm^{-1}.

3.2.3. Analytical procedures

Preparation of stock solution and working solution

The stock solution of fluoride was prepared by dissolving 0.221 g of sodium fluoride (NaF) in 1000 ml of distilled water. Working solutions were prepared by appropriate dilution from the stock solution and were kept between the ranges of 20 to 100 mg/L

Total ionic strength adjustment buffer (TISAB)

The total ionic strength adjustment buffer (TISAB) was prepared following the procedure developed by [23] Accordingly 57 ml of glacial acetic acid, 58 g of NaCl, 7 g of sodium citrate, and 2 g of EDTA were added to 500 ml of double distilled water and allowed to dissolve, and then, the pH was adjusted to 5.3 with 6 M NaOH. Finally, the solution was adjusted up to 1,000 ml in a volumetric flask with double distilled water.

Instrumentation

Fluoride ion was measured by Orion Fluoride ion selective electrode. A pH/ISE meter (OrionModel, EA 940 Expandable Ion Analyzer) was employed. The liquid phase fluoride concentration was measured according to the procedure described in the instrument's manual. The method of direct potentiometry was used, where the concentration can be read directly. The fluoride ion selective electrode was calibrated prior to each experiment in order to determine the slope by using fluoride standard solutions. The pH was measured with pH/ion meter (WTW Inolab pH/IONLevel 2, Germany) using unfilled pH glass electrode. The meter was calibrated each time measurements were being performed by using pH calibration buffers. All determinations were performed in duplicate.

3.3. Batch Adsorption Studies

All batch experiments were conducted in 500 ml Erlenmeyer flask containing 50 ml of fluoride Solution at room temperature (22± $2C^o$) to evaluate fluoride removal efficiency and capacity of the adsorbent under continuous mixing condition with magnetic stirrer. The effect of pH, initial fluoride concentration, adsorbent dose and contact time were investigated by varying any one of the parameters and keeping the other parameters constant. For each trial, a sample was periodically taken out of the flask and filtered through a0.45 µm filter paper for fluoride analysis. Then, residual fluoride concentration was measured immediately after equal volume of TISAB was added on 5 ml sample solution. All the experiments were performed in duplicate and the mean values were used.

The amount of fluoride adsorbed per unit mass of the adsorbent at any time t (q_e, mg/g), and the fluoride removal efficiency (% R, determined as the fluoride removal percentage relative to the initial fluoride concentration) of the system, was calculated as:

$$R(\%) = \frac{(C_O - C_e)*100}{C_o} \quad (6)$$

$$q_e = \frac{(C_o - C_e)\,v}{m} \quad (7)$$

WhereC_o, C_e, q_e ,V and m are initial fluoride concentration (mg/l), fluoride concentration at equilibrium (mg/l), adsorption capacity (mg/g),volume of fluoride solution (l) and weight of adsorbent (g), respectively. Blanks containing no fluoride ions were used for each series of experiments as controls.

Effect of pH

The effect of solution pH on the adsorption of fluoride onto the adsorbent was investigated by varying the initial solution pH range from 2 to 8. Before mixing the adsorbent, the pH of each fluoride solution was adjusted to the required value by adding 0.1 M NaOH or 0.1 M HCl solution. Initial fluoride concentration (20mg/l), adsorbent dosages 400g/l (0.4 g/ml) or and contact time (180 min) were kept constant during the experiment

Effect of adsorbent dose

To investigate the effect of adsorbent dose, experiments was conducted by varying adsorbent dose in the range of 0.1 to 0.04g/ml at constant initial fluoride concentration of 20 mg/l, pH of 2 and contact time (180 min)

Effect of Initial Fluoride Ion Concentration

To examine the effect of initial fluoride concentration, experiments were conducted by varying fluoride concentrations ranging from 20 to 100mg/L at constant adsorbent dose of 0.4 g/ml, pH of 2, and constant time (180 min)

Effect of Contact Time

To investigate the effect of contact time, experiments were conducted by varying time (30-210 min). Initial fluoride concentration (20 mg/L), pH of 2 and adsorbent dose (0.4g/ml) were kept constant.

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3.4. Design of Experiments

Response surface methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables. RSM can help in investigating the interactive effect of process variables and in building mathematical model that accurately describes the overall process. The most common and efficient design used in response surface modeling is the Box–Behnken design. [61]

Experimental design

A three-level four factor Box-Behnken experimental design was generated with the Design Expert 6.0.8 software. Box–Behnken statistical experiment design and the response surface methodology were employed to investigate the effects of the four independent variables on the response function. The independent variables were pH (A), initial fluoride concentrations (B) adsorbent dose (C) and Contact time (D).

Table 2 Independent factors for Box-Behnken

Factors	Unit	Levels	
		Actual(low)	Actual(high)
pH		2	6
Initial fluoride conc	mg/l	20	100
Adsorbent dose	g	10	20
Contact time	hr	1	3

The response variable, Y (F^-adsorption capacity, %) can be expressed as a function of the independent process variables pH (A),fluoride concentrations (B) adsorbent dose (C) and Contact time(D) according to the following response surface quadratic mode

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{24} BD + \beta_{34} CD \quad (8)$$

The coefficients, i.e. the model constantβ_0, the linear terms ($\beta_{1,}\beta_2, \beta_3, \beta_4$), the quadratic terms ($\beta_{11,}\beta_{22,}\beta_{33,}\beta_{44)}$and the interaction terms ($\beta_{12,}\beta_{13}, \beta_{14}, \beta_{23,}\beta_{24,}\beta_{34}$), have been estimated from the experimental results applying least square method

Isotherm modeling of fluoride adsorption

Isotherm study on adsorption provides information on the efficiency of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for adsorbate molecules. The most widely accepted surface adsorption isotherm models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration were tested with the Langmuir and Freundlich isotherm equations .Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Langmuir isotherm model

The Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as,

$$q_e = \frac{q_{\max} b\, C_e}{1+b\, C_e} \tag{9}$$

Where q_e the amount is adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/l), q_{max} and b are the Langmuir constants related to capacity and energy of adsorption, respectively.
The linear form of the Langmuir equation is represented by Equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} b} \tag{10}$$

The constants q_{max} and b can be determined from the slope of the liner plot of $\frac{C_e}{q_e}$ versusC_e. The shape of the Langmuir isotherm can be used to predict whether adsorption system is favorable or unfavorable in a batch adsorption process [18]. The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) that can be defined by the following relationship.

$$R_L = \frac{1}{1+\mathrm{b}C_O} \tag{11}$$

Where C_e is the initial concentration of fluoride (mg/L) and b is the Langmuir constant (g/L).The value of separation factorR_L, indicates the isotherms shape and the nature of the adsorption process as unfavorable (R_L>1), linear (R_L =1), favorable (0<R_L<1) and irreversible (R_L = 0) [58].

Freundlich isotherm model

The Freundlich model refers to surface heterogeneity of the adsorbent. The Freundlich isotherm has the general form,

$$q_e = K_f C_e^{\frac{1}{n}} \tag{12}$$

The linearised Freundlich adsorption isotherm can be expressed as,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{13}$$

Where K_f and n are Freundlich constants whose value depend on experimental conditions. K_f represents the adsorption capacity while $\frac{1}{n}$ is the heterogeneity factor . K_f and $\frac{1}{n}$ can be obtained from the plots of $\log q_e$ againstlog C_e . A linear plot means that the adsorption process conforms to the Freundlich isotherm. $\frac{1}{n}$ Value much less than 1 show that adsorbents are heterogeneous [18]

Effect of co–existing anions on fluoride adsorption capacity of ATSDE

The effect of anions (SO_4^{2-} Cl–, $NO_3^-$and PO_4^{3-}) on fluoride adsorption was studied in batch mode .The solutions of the required concentration of anions (0.1M) were prepared by dissolving the sodium salts of the respective anions in deionized water containing 20 mg/L fluoride. The pH of the solution was adjusted to 2. Then, 0.4g/ml of ATSDE was added and allowed to equilibrate for 3hrs under continuous mixing conditions at room temperature (22 ± 2 °C). The residual fluoride concentration was determined in the supernatant Experiments were performed in duplicate.

4. RESULTS AND DISCUSSION

4.1. Investigation of adsorption capacity of spent diatomaceous earth

The fluoride removal capacity of Spent Diatomaceous Earth (SDE) was examined by batch adsorption tests using 20 mg/L initial F concentration, 100g/l (0.1 g/ml) adsorbent dosage ratio at pH ranging from 2 to 8 and contact time 180 min. As illustrated Fig.1, spent diatomaceous earth possesses fluoride adsorption capacity throughout the pH range studied. The adsorption capacity is decreasing with increasing pH and maximum removal of fluoride is obtained at PH 2 (20%) and minimum at PH 8 (2.1).Hence, fluoride adsorption increases at low pH as the surface sites are positively charged. The reduction in fluoride adsorption at higher pH is due to negatively charged sites.

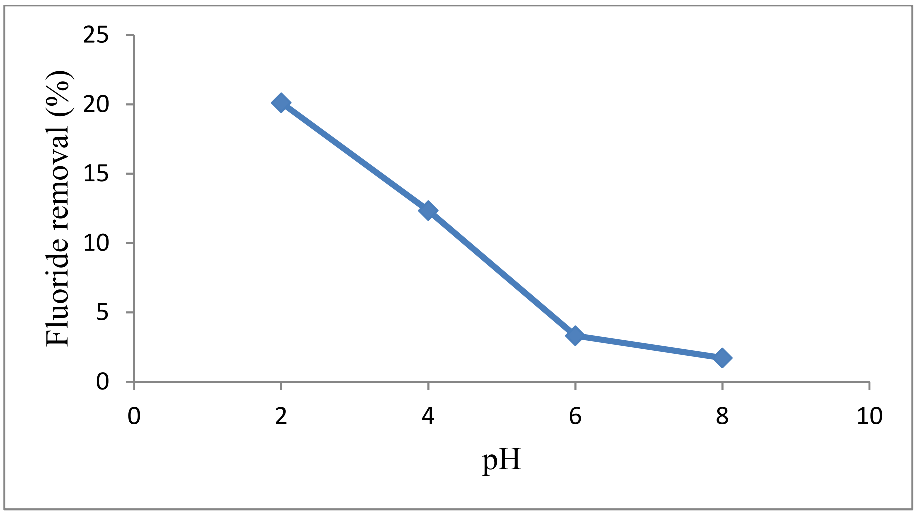

Figure 1 Effect of pH on fluoride adsorption onto sent diatomaceous earth (initial fluoride concentration=20 mg/l, adsorbent dose=100g /l and contact time=180 min)

4.2. Effect of Acid Treatment Time

Effect of acid-treatment time on Spent Diatomaceous Earth (SDE) was examined by batch adsorption tests using 20 mg/l initial fluoride concentration, 100g/l (0.1 g/ml) adsorbent dosage ratio at pH 2 for time intervals (30-210 min) of SDE exposure to 0.1 M HCl. As it can be seen from Figure.2 fluoride removal efficiency of spent diatomaceous earth is increasing with increasing time of acid activation. It can also be seen that fluoride removal efficiency is higher with time of acid activation from 30- 180 min. There was no significant change in fluoride uptake of the material when acid pre-treatment time was increased above 180 min The rapid increase in fluoride adsorption capacity of the material on pre-treatment with the acid showed that when the adsorbent is placed in the acid, the surface sites in the materials were quickly protonated increasing the overall surface positive charge and potential for fluoride adsorption The 180 min contact time of spent diatomaceous earth with acid was used for further study

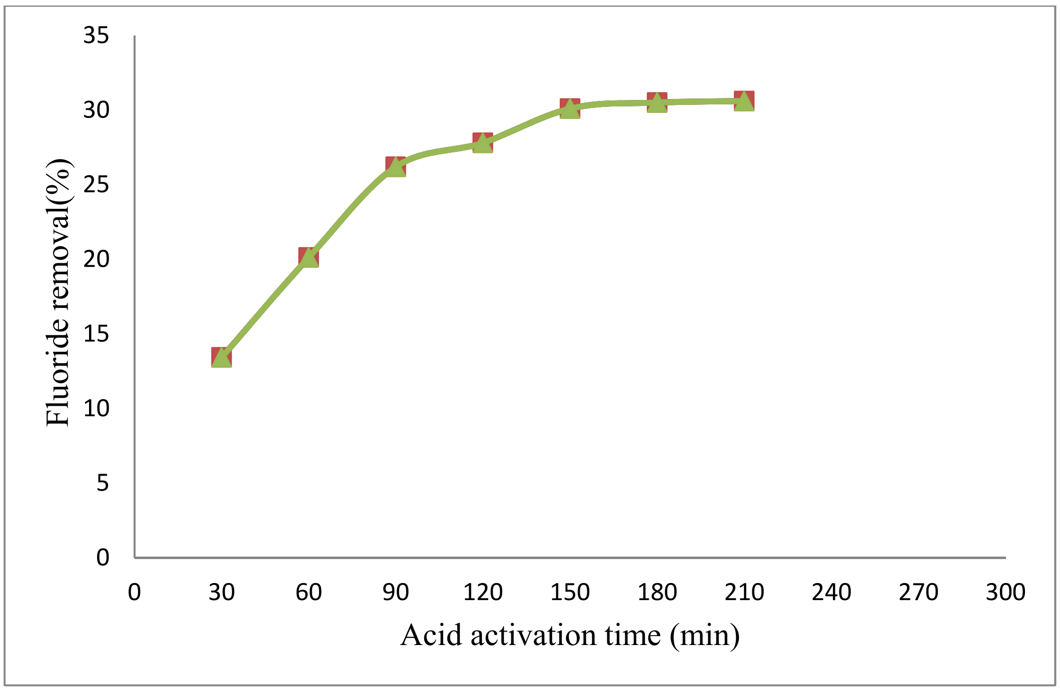

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Figure 2 Effect of time of acid activation on fluoride adsorption onto ATSDE

Characterization of samples

The chemical compositions of the spent and acid treated spent diatomite samples expressed as weight percentage are reported in Table 3.The main components of the natural raw diatomite are SiO_2 and Al_2O_3 with few amounts of theF_2O_3, MgO and CaO contents. After the acid treatment, the SiO_2, CaO, and MgO decrease, at the same time the $Al_2O_3$and F_2O_3increase. The slight decrease of SiO_2 ratio can be ascribed to the fact that the silica is relatively resistant to acid attack whereas Mg and Fe salts are more soluble in acidic conditions. Calcium is mainly in the form of carbonate, which can be decomposed easily in acidic media. Thus, the content of CaO decreased markedly after acid treatment of spent diatomaceous earth [62].The removal of impurities, replacement of exchangeable cations (K^+, Na^+, and Ca^{2+}) with hydrogen ions, leaching of Al^{3+} andFe^{3+}, and from the octahedral and tetrahedral sites which exposes the edges of the clay particles [63]

Table 3 Chemical composition of raw and acid treated spent diatomaceous earth

Chemical composition	Percentage	
	Raw DE	ATSDE
SiO_2	89	88.04
Al_2O_3	4.1	4.48
Fe_2O_3	1.5	1.84
MgO	0.3	0.26
Cao	0.6	<0.01
Other oxide	4	3.15
Loss of ignition	1	0.92

FTIR analysis

The FTIR spectrum of ATSDE is showed in Figure.3.The broad band at about 3430 cm^{-1} was attributed to the stretching vibration of the hydroxyl of the physically adsorbed water molecules [64]. The band at 1100 cm^{-1} is assigned to the of siloxane (Si O-Si) anti-symmetric stretching vibration. The band at 780 cm^{-1} due to the stretching mode of oscillation of OH in the Si–OH. Other band at 474 cm−1 is also characteristic of silica [20]

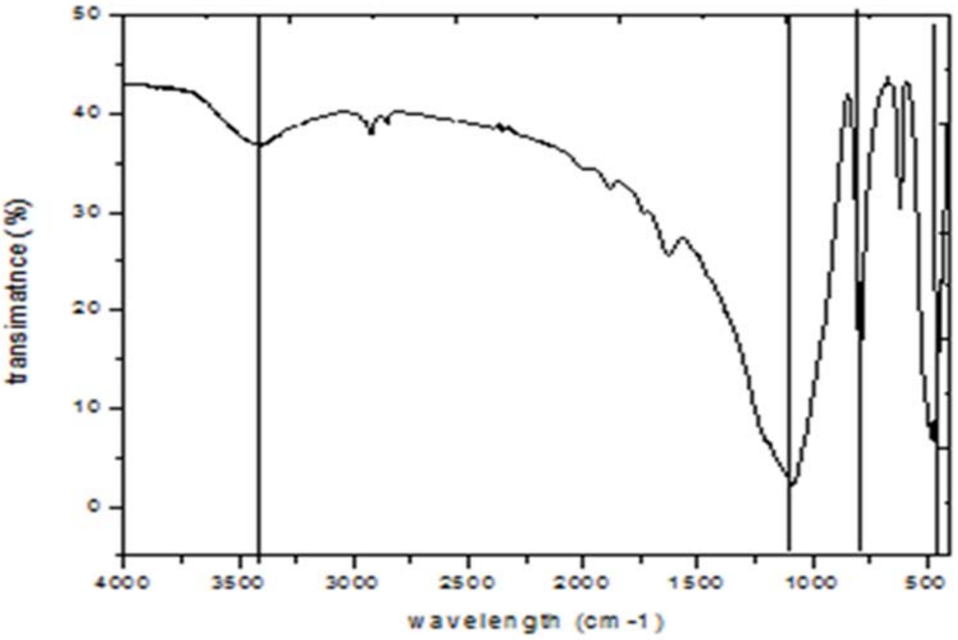

Figure 3 FTIR spectra of ATSDE, in 4000–400 cm−1 region.

Determination of zero point charge

Figure 4 shows that there is a common intersection point for the potentiometric titration curves of three different mass of acid treated spent diatomaceous earth mixed in 0.1 M NaNO3 solutions and the titration curve of a blank solution. The pH of this common intersection point corresponds to PZC value and it was found to be 2.42.

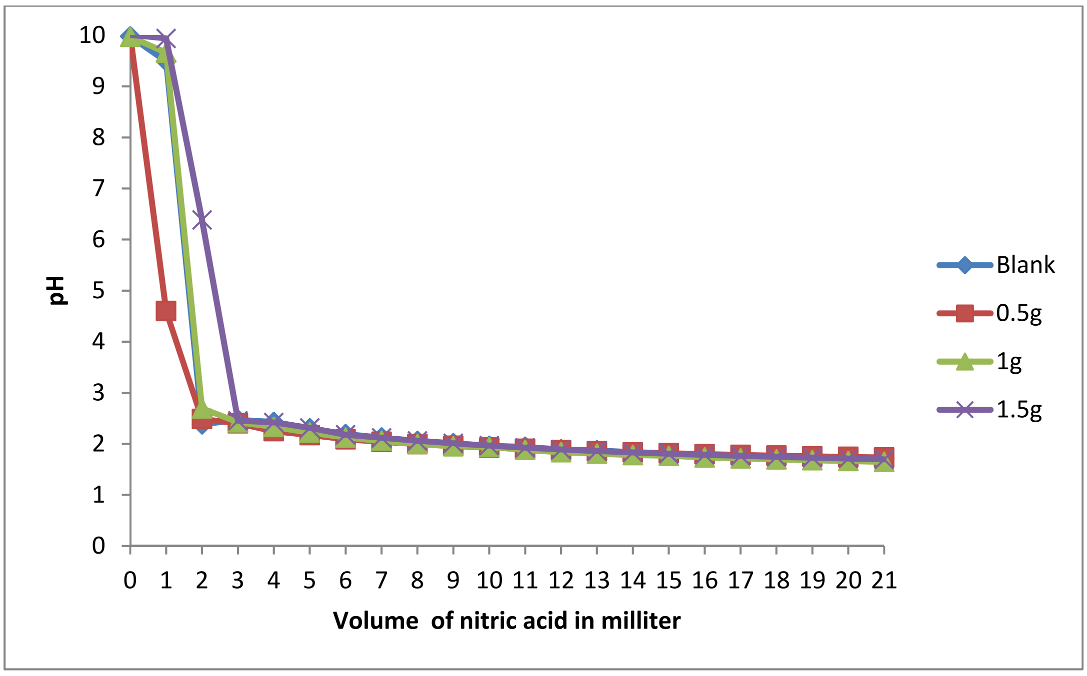

Figure 4 potentiometric mass titration curves of acid treated spent diatomaceous earth

4.2.1 Effect of pH

The pH of the solution is one of the most critical parameters in the adsorption process, which affects surface charge of the adsorbent material and the degree of ionization and specification of adsorbate [58] .The effect of pH on the removal efficiency of fluoride ion was studied at different pH ranging from 2.0 to 8. As it can be seen from Figure5, decrease in the fluoride ion removal occurred when the pH value of the solutions changed from 2.0 to 8. The maximum adsorption of fluoride ions are obtained at pH 2.0. So pH 2.0 was selected as optimum pH for fluoride ion adsorption onto ATSDE. Again the FTIR spectral analysis indicates the presence of OH functional groups onto adsorbent surface. OH^{-} groups are protonated at lower pH and thereby facilitate the approach of negatively charged fluoride ions to the surface of the adsorbent which results in higher uptake of fluoride ions. With decrease in acidity of the solution, the functional group on the adsorbent surface become de-protonated resulting in an increase in the negative charge density on the adsorbent surface and restricts the binding of fluoride anions. The decrease in fluoride ion removal efficiency at higher pH may also be attributed to the abundance of OH- ions which compete with fluoride anions at higher PH. Similar trend has been reported for fluoride removal using diatomaceous earth. [18] and montmorillonite clay [19].

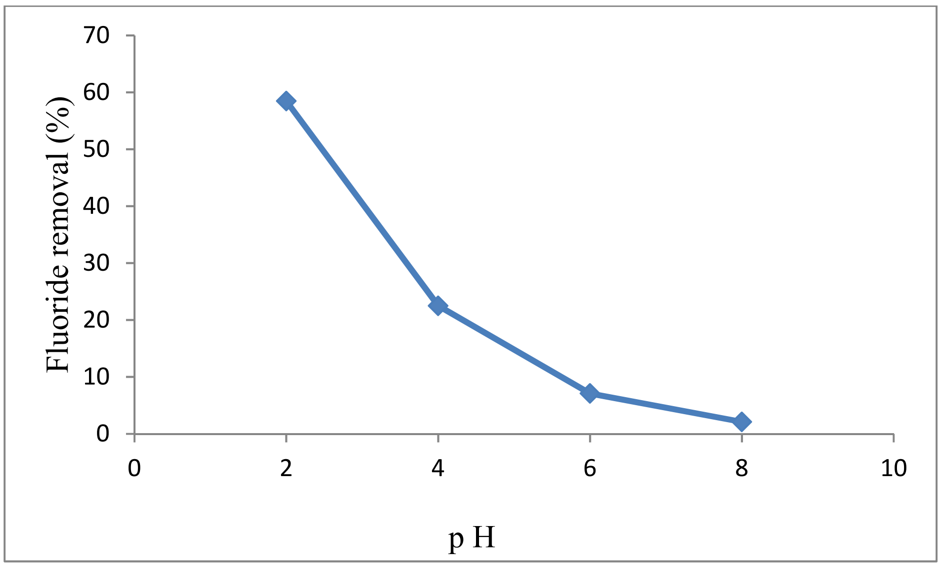

Figure 5 Effect of solution pH on fluoride adsorption onto ATSDE (initial fluoride concentration=20 mg/l, adsorbent dose=400g / ml and contact time= 180 min)

Fluoride removal at the adsorbent surface at pH<pHpzc was expected to be by electrostatic attraction of the fluoride ions by the positively charged surface. The more electropositive the surface was the more the attraction for fluoride .This explains why the maximum fluoride removal (58.47.0%) occurred at pH 2.0 as shown in the Figure.5.

.Since the ATSDE contains metal oxides (Si, Al and Fe), when it was added to an aqueous solution, the surface silanol would be protonated to develop a surface charge. The existence of surface charge depends on the pH. Adsorption of fluoride by the oxide species can be modeled as the following two-step ligand exchange reaction [17]

$$\mathrm{M-OH+H^{+}\rightarrow MOH_2^{+}} \quad (14)$$

$$\mathrm{MOH_2^{+}\ +F^{-}\ \rightarrow MF\ +OH^{-}} \quad (15)$$

Where M is Si, Al, Fe and the adsorption was more favorable at low pH values.

4.2.3. The effects of adsorbent dose

The effect of adsorbent dose on the removal of fluoride at optimum pH (2) is shown in Figure.6.The effect of varying adsorbent mass while maintaining the adsorbate volume and concentration constant was studied as follows: 5, 10, 15, and 20-gram of the ATDE were placed in 50 ml of the adsorbate solution containing 20 mg/L of F and contact time 180 min. The percentage F removal was determined and plotted against the mass of the adsorbent and the results presented in Figure 6

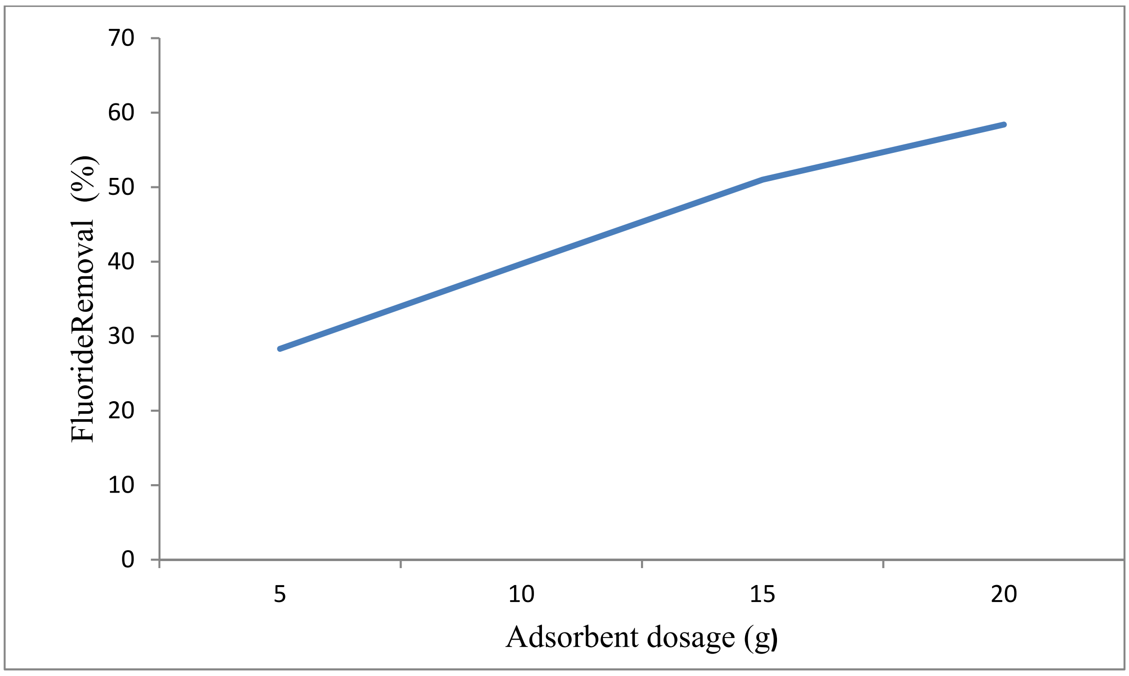

Figure 6 Effect of adsorbent dosage on fluoride adsorption onto ATDE (initial fluoride solution=20mg/l,pH = 2 and contact time 180 mi)

As the Figure.6 illustrates, there was a considerable rise in the percent fluoride removal with increase in the mass of sorbent from 5gram to 20 gram. The overall percentage F removal from solution rapidly increased with increase in ATDE dosage.58.4% F adsorption could be achieved at 20 g per 50ml ATDE dosage. The adsorbent dosage ratio of 400g/l (0.4 g/ml) was therefore adopted in the rest of the tests. The increase in per cent fluoride removal was due to increase in the \number of adsorption sites as the dosage increased. Similar findings for fluoride adsorption onto other adsorbent have been reported by other investigator. [16.20]

4.2.4. The effects of initial fluoride concentration

The effects of the initial fluoride concentrations on the removal of fluoride were studied by varying the initial fluoride concentrations in the range 20mg/l- 100mg/l at a constant contact time and adsorbent dose

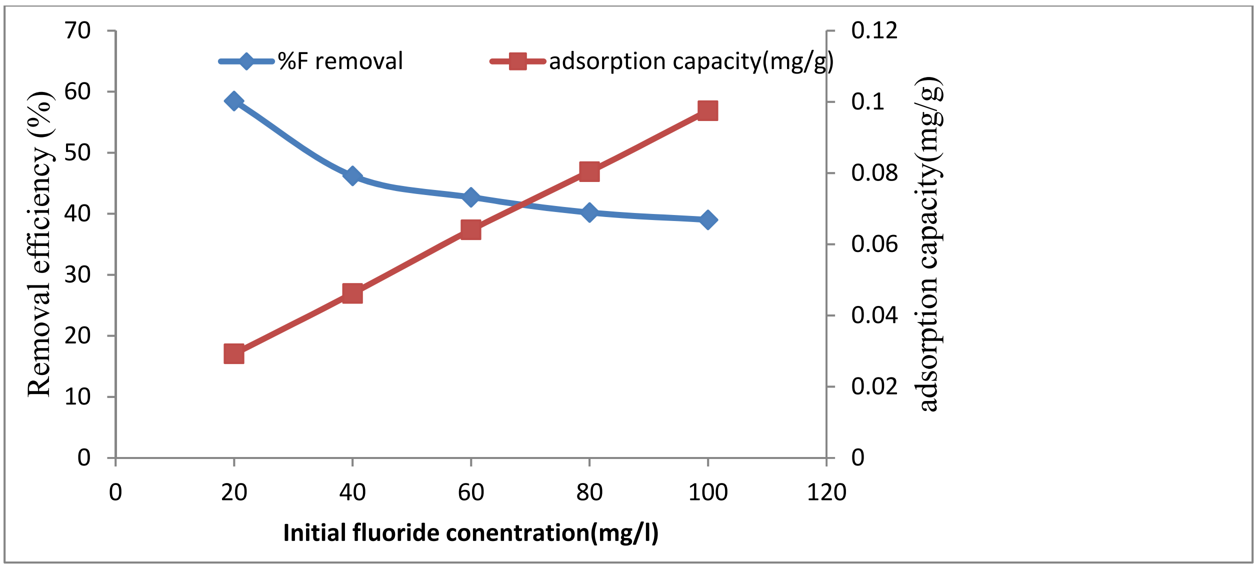

Figure 7 Effect of the initial fluoride concentration on fluoride removal by ATSDE (PH =2, adsorbent dose= 400g/l (0.4g/ml) and contact time=3 hr)

In Figure 6.it can be seen that percent fluoride removal efficiency decreases with increasing initial fluoride concentration for a constant adsorbent dose and contact time. The reason was that the capacity of the adsorbent materials gets exhausted sharply with the increase in initial fluoride concentration. This was due to the fact that for a fixed adsorbent dose, the total available adsorption sites were limited, which became saturated at a higher concentration. Similar trend has been reported for fluoride removal by red soil [20]. But adsorption capacity increase with increasing initial fluoride concentration. Due to increasing concentration gradient, acts as increasing driving force to overcome all mass transfer resistances of the fluoride between the aqueous and solid phase, leading to an increasing uptake capacity until sorbent saturation is achieved. Similar trend has been reported for fluoride removal by ATDE [16]

4.2.5. Effect of contact time

It is essential to investigate the effect of contact time required to reach equilibrium for designing batch adsorption experiments. The fluoride removal capacity on ATSDE was conducted by varying contact time (30–210 min) with a dose of 0.4 g/ml at PH=2. As illustrated in figure8, the rate of fluoride adsorption was very rapid during the first 180 min, and thereafter, the rate of fluoride adsorption remained constant. There was no significant increase in adsorption after about 180 min. The adsorption process attained equilibrium after 180min.The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface

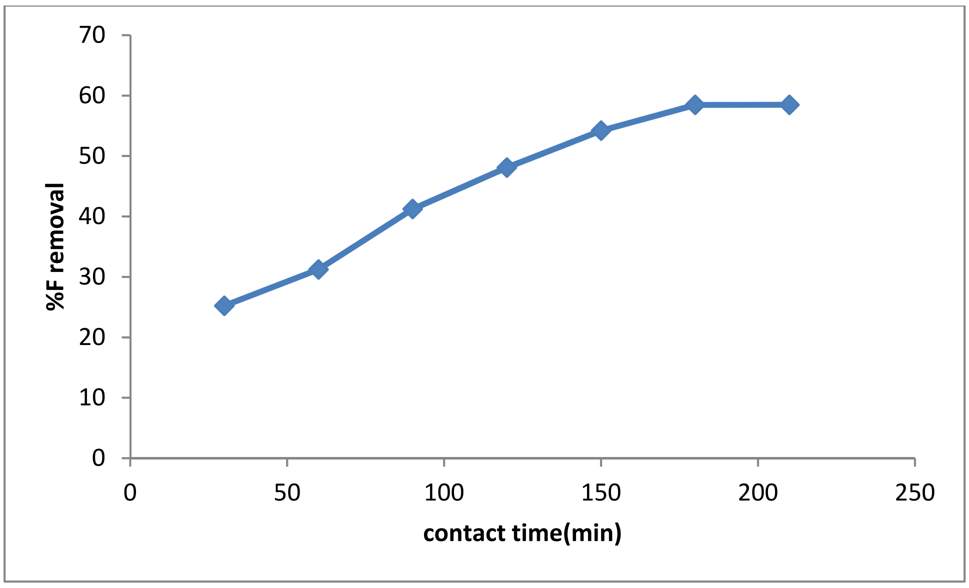

Figure 8 Effect of contact time on fluoride adsorption on ATSDE (initial fluoride solution=20mg/l, at PH =2 and adsorbent dose=400g/l (0.4g/ml)

4.3. Experimental runs

Box–Behnken design is used to predict the fluoride adsorption rate. Experimental Box-Behnken design and results on adsorption of fluoride by ATSDE is presented in Table6

Table 4 Experimental design and response of experimental

Std	Run	Block	Factor1 pH	Factor 2 initial f con mg/l	Factor 3 adsorbent dose g	Factor 4 contact time hr	Response F removal %
1	19	Block 1	2.00	20.00	15.00	2.00	41
2	29	Block 1	6.00	20.00	15.00	2.00	16.5
3	3	Block 1	2.00	100.00	15.00	2.00	30
4	27	Block 1	6.00	100.00	15.00	2.00	3
5	25	Block 1	4.00	60.00	10.00	1.00	13
6	8	Block 1	4.00	60.00	20.00	1.00	16
7	13	Block 1	4.00	60.00	10.00	3.00	14.1
8	2	Block 1	4.00	60.00	20.00	3.00	17.5
9	21	Block 1	2.00	60.00	15.00	1.00	32.2
10	18	Block 1	6.00	60.00	15.00	1.00	9.5

11	26	Block 1	2.00	60.00	15.00	3.00	39.8
12	4	Block 1	6.00	60.00	15.00	3.00	9.65
13	28	Block 1	4.00	20.00	10.00	2.00	19
14	14	Block 1	4.00	100.00	10.00	2.00	5
15	11	Block 1	4.00	20.00	20.00	2.00	22
16	22	Block 1	4.00	100.00	20.00	2.00	7
17	23	Block 1	2.00	60.00	10.00	2.00	33
18	24	Block 1	6.00	60.00	10.00	2.00	8
19	1	Block 1	2.00	60.00	20.00	2.00	40
20	12	Block 1	6.00	60.00	20.00	2.00	10
21	6	Block 1	4.00	20.00	15.00	1.00	18
22	7	Block 1	4.00	100.00	15.00	1.00	6.7
23	20	Block 1	4.00	20.00	15.00	3.00	21
24	15	Block 1	4.00	100.00	15.00	3.00	7
25	9	Block 1	4.00	60.00	15.00	2.00	18.5
26	17	Block 1	4.00	60.00	15.00	2.00	19.87
27	16	Block 1	4.00	60.00	15.00	2.00	20
28	5	Block 1	4.00	60.00	15.00	2.00	19.9
29	10	Block 1	4.00	60.00	15.00	2.00	19.5

4.3.1. Design Summary

Design summary shows information of experimental design parameters, designing method used, and model fitting to the experiment response, constraints region of selected parameters with their units and the coded value of design

Table 5 Design Summary

Study Type	Response Surface	Experiments	29				
Initial Design	Box Behnken	Blocks	No Blocks				
Design Model	Quadratic						
Response	Name	Units	Obs	Minimum	Maximum	Trans	Model

Y1	F removal	%	29	3.00	41.00	None	Quadratic
Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	pH		Numeric	2.00	6.00	-1.000	1.000
B	Initial F con	mg/l	Numeric	20.00	100.00	-1.000	1.000
C	adsorbent dose	g	Numeric	10.00	20.00	-1.000	1.000
D	contact time	hr	Numeric	1.00	3.00	-1.000	1.000

4.3.2. Development of regression model

Box–Behnkendesign has been used to developed correlation, between the adsorption of fluoride from aqueous solution using acid treated diatomaceous earth. Model was selected based on highest order polynomials, where the additional terms were significant and model were not aliased based. Second order quadratic polynomial model was selected to represent the relations between the selected parameters and the required response

. Experiments were performed according design given by software, 29 runs performed to have responses (%) adsorption. Model represented by equation variables having coded

$$Y (\%) = +19.55-13.28 * A-6.57* B+1.70* C+1.14 * D +6.01* A^2-3.54 * B^2 - 2.49 * C^2-2.51D^2 - 0.62 * A * B-1.25 * A * C-1.86* A * D -0.25 * B * C-0.67 * B * D+0.10 * C \; D \quad 1 \qquad (16)$$

From Eq. (16), it can be seen that adsorbent dose and contact time have positive effect on fluoride adsorption compared to pH and initial concentration, which have a negative effect on the fluoride adsorption

In terms of actual factors:

$$\text{Fluoride removal} = +12.83685 -14.46267 * PH +0.018520 * \text{Initial fluoridconc} +3.86490* \text{adsorbent dose}+15.61633 * \text{contact time} +1.5036*^{PH^2}-2.21349E-005*\text{Initialfluorideconc}^2 -0.099663* \text{adsorbent dose}^2 -2.51033* \text{contact time}^2$$

-7.81250E-004*PH*Initialfluorideconc

-0.12500 * PH * adsorbent dose-0.93125 * PH * contacttime

-1.25000E-004*Initialfluorideconc*adsorbentdose

-1.68750E-003*Initialfluorideconc*contacttime

+0.020000 * adsorben dose * contact time (17)

4.3.3. Statistical analysis

The coefficient of determination (R^2) of the model was 0. 0.9949, which indicated a good fit between predicted values and the experimental data points (Fig. 9.and Table.6). In addition, this implies that 99.49% of the variations for percent fluoride adsorption are explained by the independent variables, and this also means that the model does not explain only about 0.5% of variation. Predicted R^2 is a measure of how good the model predicts response value. The adjusted R^2 and predictedR^2 should be within approximately 0.20 of each other to be in reasonable agreement .If they are not, there may be a problem with either the data or the model In this work, the predicted R^2 of 0.9728 is in reasonable agreement with the adjusted R^2 of 0.9899, this signifies runs were performed successfully no problem with data. Adequate Precision measures the signal to noise ratio and compares the range of the predicted values at the design points to the average prediction error. The ratio greater than 4 is desirable and indicates adequate model discrimination. In this work the ratio is found to be 51.248, which indicates the reliability of the experiment data. The coefficient of variation (CV= 5.82) and standard deviation (SD = 1.08) indicate the degree of precision (Table.6). The low values of CV and SD show the adequacy with which the experiment is conducted. The models have high R^2 value, significant F-value, an insignificant lack-of-fit P-value and low standard deviation and coefficient of variance. These results indicate the high precision in predicting the fluoride removal efficiency by ATSDE. Therefore; the models were used for further analysis.

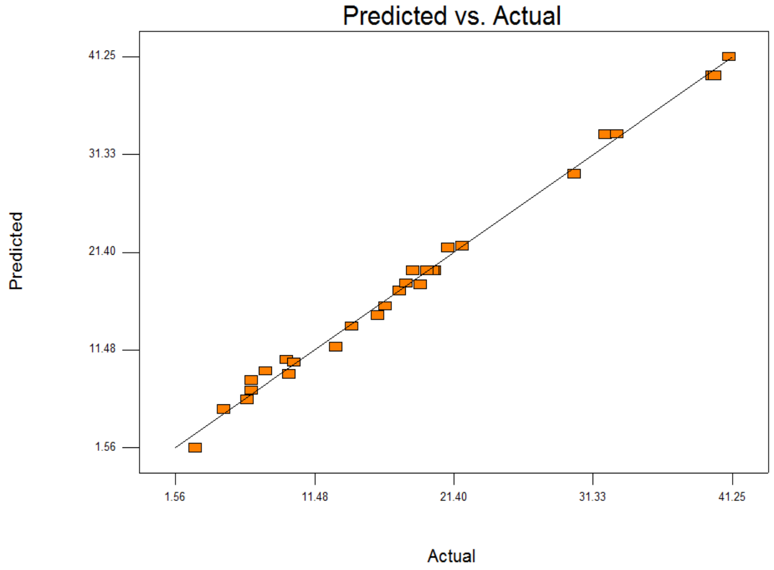

Figure 9 Plot of the experimental and predicted responses

Table 6 Analysis of R squared values, S.D and CV for adsorption model

R-squared	0.9949
AdjR-squared	0.9899
PreR-squared	0.9728
Adeq precision	51.248
Std,Dev	1.08
CV	5.82

Analysis of variance (ANOVA)

Model fitting in the form of analysis of variance (ANOVA).The analysis of variance is essential to test significance and adequacy of the model. It subdivides the total variation of the results in two sources of variation, the model and the experimental error, shows whether the variation from the model is significant when compared to the variation due to residual error The Fisher's F-test value, which is the ratio between the mean square of the model and the residual error, performs this comparison [61]The Model F-value of 196.55 in the ANOVA infer that the model was significant and that there is only a chance of 0.01% that a Model F-value this large could occur due to noise. In addition, the p-value was found to be < 0.0001, which indicated that the model was highly statistically significant. The ''Lack of Fit Test'' compares the residual error to the pure error from replicated design points. The "Lack of Fit F-value" of 3.83 implies the Lack of

Fit is not significant relative to the pure error. There is a 10.34% chance of occurrence of noise, indicating significance of the model. The significance of each term was determined by p-value (Prob>F), which is listed in Table 9. As seen in this table that the terms A, B, C, D, A^2, B^2, C^2, D^2, AC, AD ,were significant, with very small p-values ($p < 0.05$). The other term coefficients were not significant ($p > 0.05$)

Table 7 Analysis of variance(ANOVA) for Response Surface Quadratic Model

Source	Sum of squares	DF	Mean square	F value	Prob>F	
Model	3191.15	14	227.94	196.55	< 0.0001	Significant
A	2116.04	1	2116.04	1824.63	< 0.0001	
B	517.45	1	517.45	446.19	< 0.0001	
C	34.68	1	34.68	29.90	< 0.0001	
D	15.53	1	15.53	13.39	0.0026	
A2	234.66	1	234.66	202.34	< 0.0001	
B2	81.36	1	81.36	70.15	< 0.0001	
C2	40.27	1	40.27	34.72	< 0.0001	
D2	40.88	1	40.88	35.25	< 0.0001	
AB	1.56	1	1.56	1.35	0.2652	
AC	6.25	1	6.25	5.39	0.0359	
AD	13.88	1	13.88	11.96	0.0038	
BC	0.25	1	0.25	0.22	0.6496	
BD	1.82	1	1.82	1.57	0.2305	
CD	0.040	1	0.040	0.034	0.8553	
Residual	16.24	14	1.16			
Lack of Fit	14.70	10	1.47	3.84	0.1034	Not significant
Pure Error	1.53	4	0.38			
Cor Total	3207.39	28	1.16			

4.4. Interaction Effects of Variables on Fluoride adsorption capacity of acid treated spent diatomaceous earth

Effect of the selected parameters on the removal of fluoride by acid treated diatomaceous earth as well as the interaction effect between them was expressed in 3D response surface diagram. The response surface plots of the second-order polynomial equation with two variables were kept constant and the other two varying within the determined experimental ranges

4.4.1. The effects of pH and initial fluoride concentration

The interaction effect between pH and initial fluoride concentration is represented by three dimensional response surfaces (Fig.10) .The relation was investigated at constant time(2 hr) and adsorbent dose(15g) As it can be seen from figure, highest fluoride removal was obtained at lower pH of 2 and high initial fluoride concentration. The lowest removal was obtained at higher pH of 6 and at high initial fluoride concentration .This observation can be explained on the basis of zero point of charge for adsorbent.

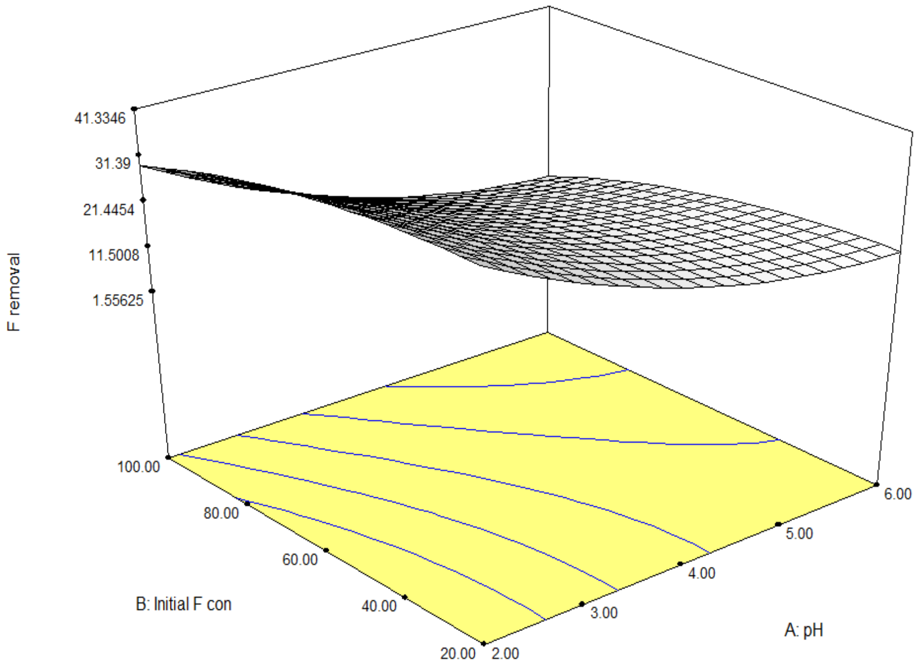

Figure 10 3D surface plot of combined effect of pH and initial fluoride con (mg/l) on percentage adsorption

4.4.2. The interaction effects of contact time and initial fluoride concentration

The interaction effect between contact time and initial fluoride concentration is represented by three dimensional response surfaces. The relation was investigated at constant pH=4 and adsorbent dose (15g).The removal efficiency decrease with increasing the initial fluoride concentration at any given time as shown in the response surface diagram. The highest fluoride removal was obtained at lower fluoride concentration and maximum contact time. This is attributed to availability of active adsorption sites at lower fluoride concentration, while increasing initial fluoride concentrations provide more fluoride ions, however the fixed amount of adsorbent has a fixed number of adsorption sites

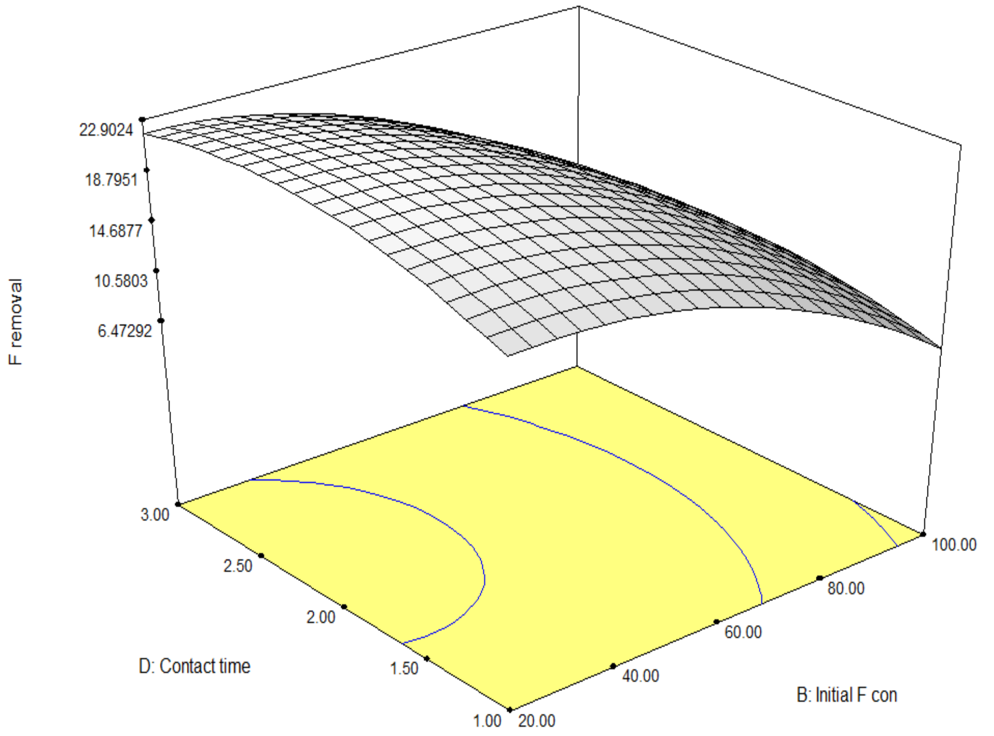

Figure 11 3D surface plot of combined effect of contact time and initial fluoride con(mg/l) on fluoride removal

4.4.3. The interaction effects of adsorbent dose and initial fluoride concentration

The interaction effect between adsorbent dose and initial fluoride concentration is represented by three dimensional response surfaces (Figure12). The relation was investigated at constant pH=4 and constant contact time, 2hours.The highest fluoride removal was obtained at higher dose and at low fluoride concentration and low removal was obtained at low adsorbent dose and higher initial fluoride concentration

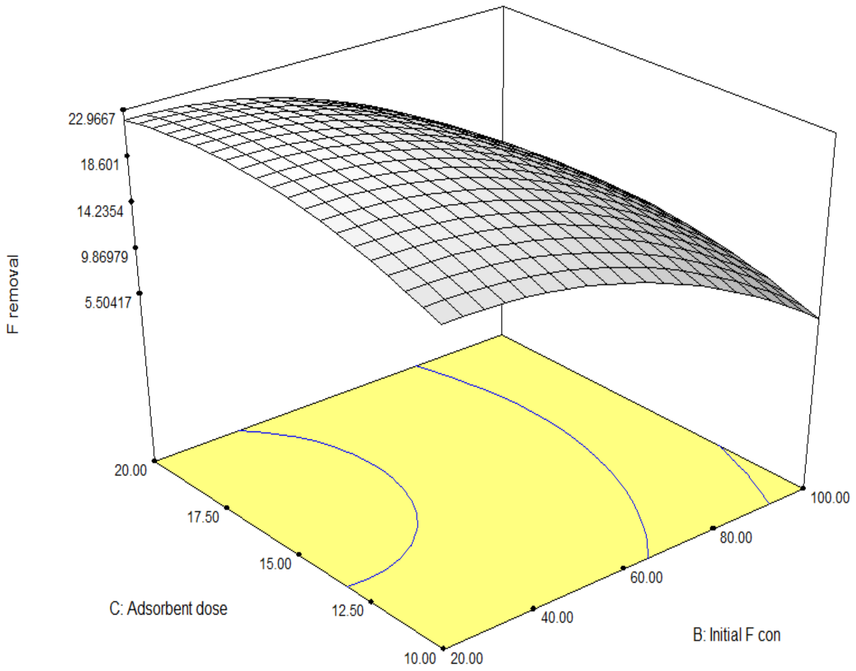

Figure 12 3D surface plot of combined effect of adsorbent dose and initial fluoride con (mg/l) on percentage adsorption

4.4.4. The interaction effects of pH and contact time

The interaction effect between PH and contact time is represented by three dimensional response surfaces (Fig.13).The relation was investigated at constant adsorbent dose (15g) and initial fluoride concentration (60mg/l). The removal fluoride is increasing with decreasing pH and increasing contact time. The maximum fluoride removal was obtained at minimum pH of 2 and maximum contact time. The low fluoride removal was obtained at high pH of 6 and maximum contact time

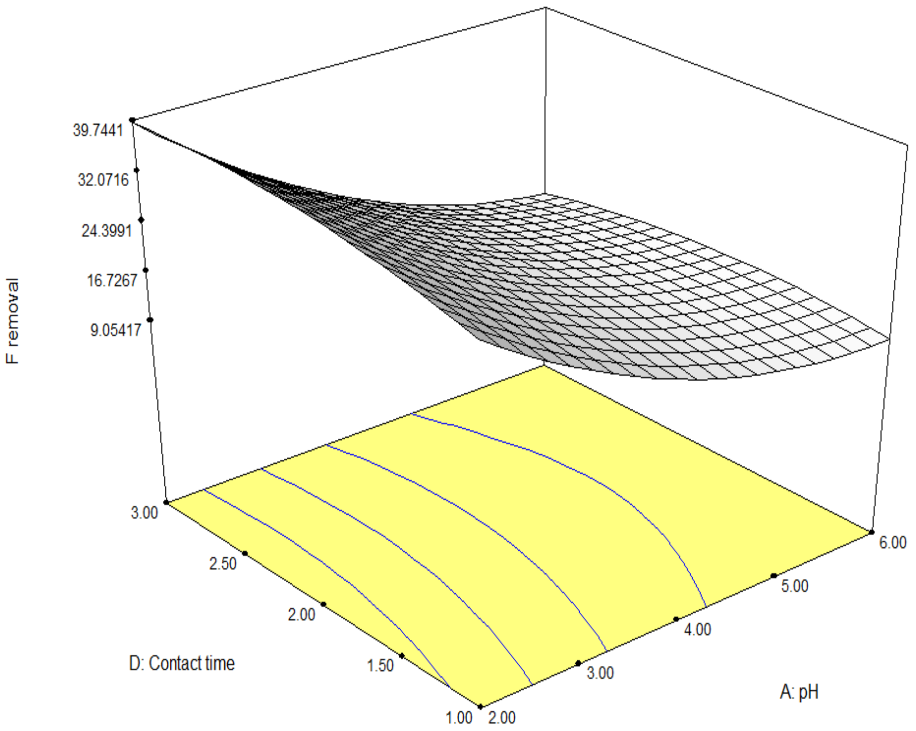

Figure 13 3D surface plot of combined effect of contact time and pH on fluoride removal

4.4.5. The interaction effects of pH and adsorbent dose

The interaction effect between PH and adsorbent dose is represented by three dimensional response surfaces (Fig.14).The relation was investigated at constant adsorbent dose (15g) and initial fluoride concentration (60mg/l).The maximum fluoride removal was obtained at low pH of 2 and maximum adsorbent dose. The low fluoride removal was obtained at high pH of 6 and maximum adsorbent dose

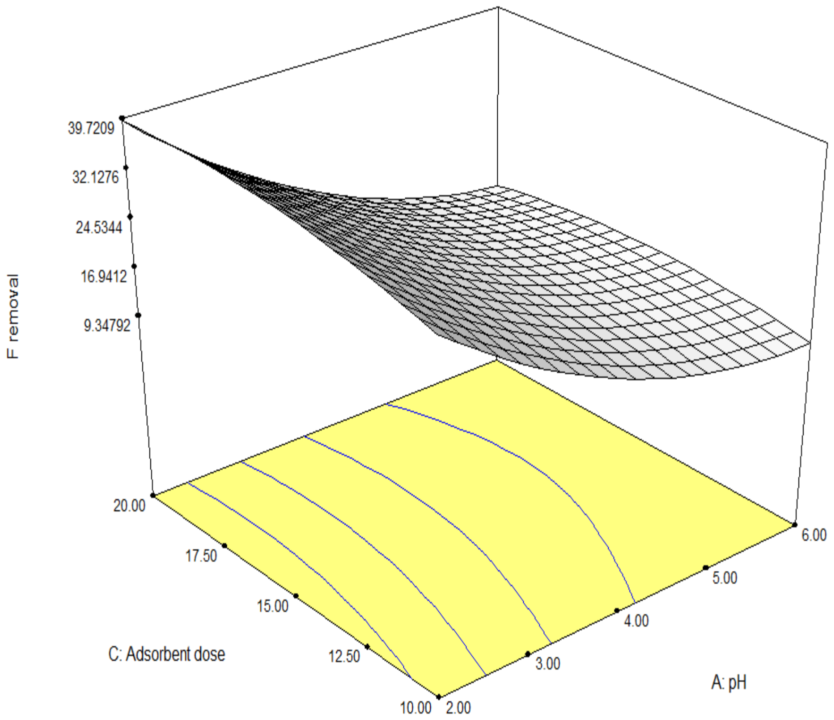

Figure 14 3D surface plot of combined effect of contact time and pH on fluoride removal

4.5. Optimization

By using numerical optimization, a desirable value for each input factor and response can be selected. The possible input optimizations that can be selected include: the range, maximum, minimum, target, none (for responses) and set so as to establish an optimized output value for a given set of conditions. In this study, the input variables were given specific ranged values, whereas the response was designed to achieve a maximum (Table.8). Using these conditions, the maximum achieved fluoride removal efficiency was 43.1906% (Figure15) at an initial pH of 2.02, fluoride concentration of 24.06 mg/L, adsorbent dose of 18.83 g, and contact time of 2.95h. The confirmatory experiment showed a fluoride removal efficiency of 42.94% under optimal conditions compared with the fluoride removal percent of 43.1906% obtained by the model. This indicates the suitability and accuracy of the model.

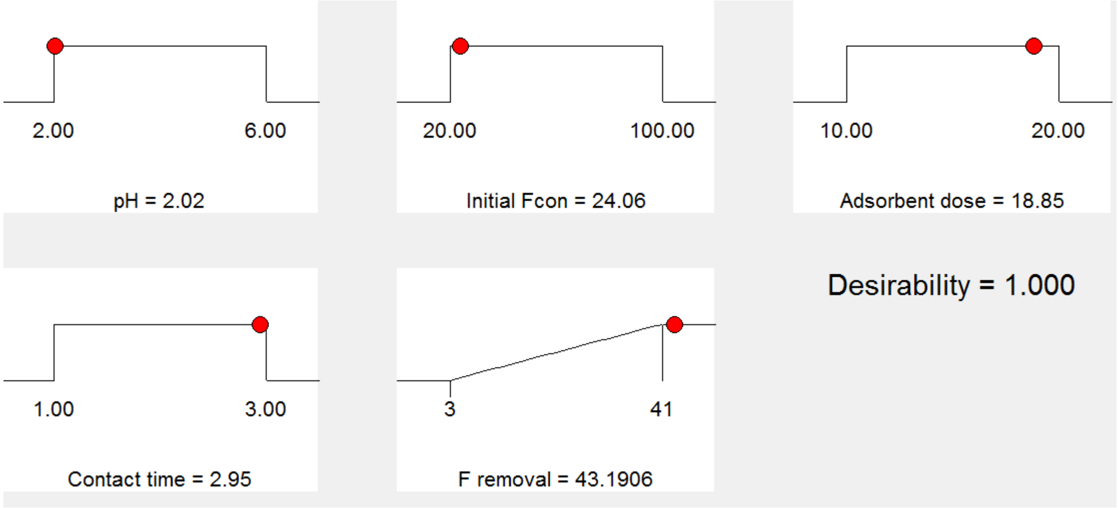

Figure 15 Desirability ramp for optimization

Table 8 selection of factors and goal for optimization for ATSDE

Name	Goal	Lower limit	Upper limit
PH	Is in range	2	6
Initial fluoride concentration(mg/l)	Is in range	20	100
Adsorbent dose(g)	Is in range	10	20
Contact time(h)	Is in range	1	3

4.6. Adsorption Isotherm

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. In the present study, Langmuir and Freundlich isotherm models were used to describe the equilibrium data. Adsorption isotherm experiments were conducted using an adsorbent dose of 400g/l (0.4 g/ml) and varying initial fluoride concentrations within the range between 20and 100 mg/L at constant pH of 2 and contact time 3hours.

The linear plot of $\frac{C_e}{q_e}$ versus C_e (Figure 16) indicates the applicability of Langmuir adsorption isotherm. The Langmuir isotherm model showed excellent fit to the experimental data with the 0.936 correlation coefficient (Table 9).

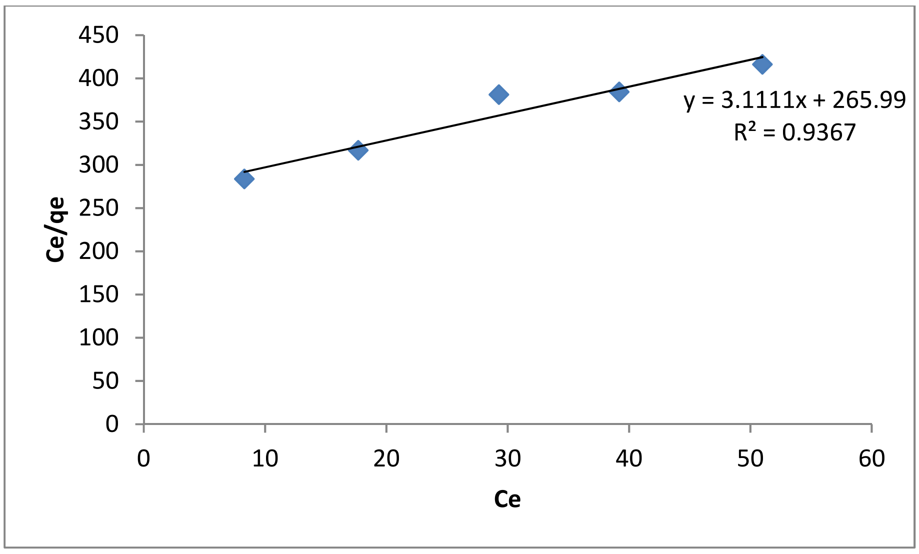

Figure 16 Langmuir adsorption isotherm for fluoride adsorption on ATSDE

Table 9 Langmuir and Freundlich adsorption constants

constants	Langmuir isotherm	Constants	Freundlich isotherm
q_{max}(mg/g)	0.321	Kf(mg/g)	0.0075
b(l/mg)	0.0117	1/n(l/mg)	0.783
R^2	0.936	R^2	0.997

Adsorption is deemed favored for RL values less than one. Table 10shows that for the adsorption Of fluoride on to ATSDE, the adsorption is always favored for the initial fluoride concentrations tested.

Table 10 value of separation factor for various initial concentrations

Initial fluoride concentration (mg/l)	Separation factor (R_L)
20	0.81
40	0.68
60	0.58
80	0.51
100	0.46

The linear plot of $\log q_e$ versus $\log c_e$ (Figure17) indicates the applicability of the Freundlich adsorption isotherm. The Freundlich isotherm model showed also fit to the experimental data with the 0.996correlation coefficient. It is therefore evident from the result that the fluoride adsorption onto ATSDE is a multi-site adsorption. The low value of 1/n (0.783) is indicative of the heterogeneity of the surface of ATSDE (Table11)

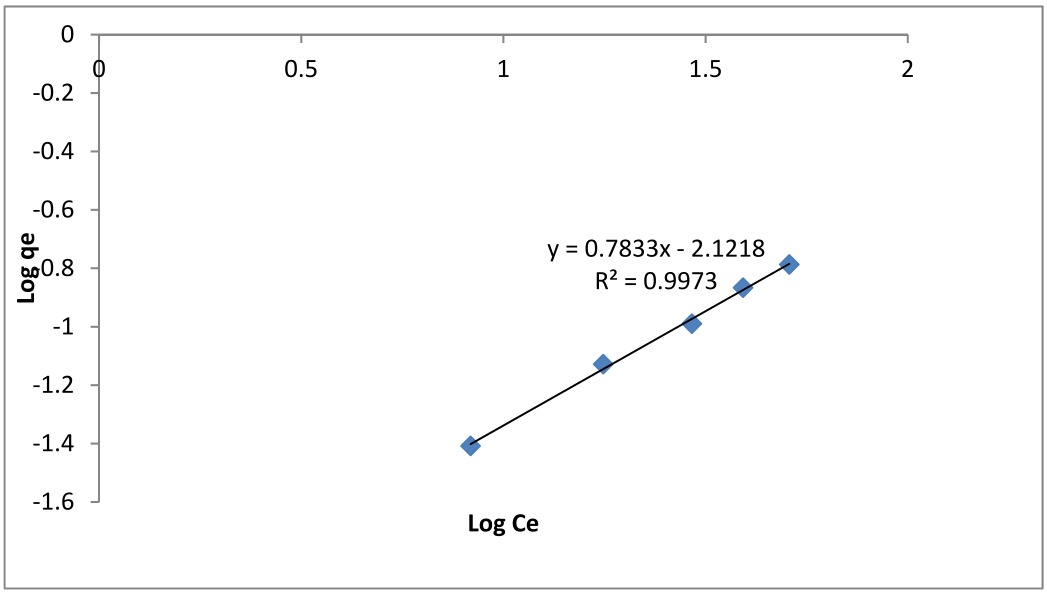

Figure 17 Freundlich adsorption isotherm for fluoride adsorption on ATSDE

Langmuir F adsorption capacity (q_{max}) was compared with those of other low-cost adsorbents in the literature and presented in Table 13

Table 11 Comparison of ATSDE with that of various low-cost adsorbents

Adsorbent	q_{max}(mg/g)	Reference
Fired clay	0.2	[22]
Raw kaolinite	0.120	[30]
Natural earth material(E1)	0.067	[31]
Bleaching powder	0.1308	[20]
ATSDE	0.321	This work

From the above table, ATSDE has higher adsorption capacity compared to the other low adsorbents except ATDE which has amount of aluminum oxide which have the better potential as sorbents for fluoride from aqueous solutions [20.27]

4.7. Effect of other anions

The effect of other potential competing anions including .chloride, nitrate, phosphate and sulphate on fluoride adsorption by acid treated spent diatomaceous earth was evaluated and the results presented in Figure 18. As can be seen from graph nitrates, sulphates and phosphates ions have no interference with fluoride removal on acid treated spent diatomaceous earth. The chloride had significant effect on fluoride removal. This is due to having a smaller radius and less steric hindrance than other anions, had higher mobility in solution and therefore competes more effectively with fluoride for adsorptive sites in acid treated spent diatomaceous earth thereby reducing fluoride adsorption more strongly. Similar trend has been reported for fluoride removal using acid treated diatomaceous earth [16]

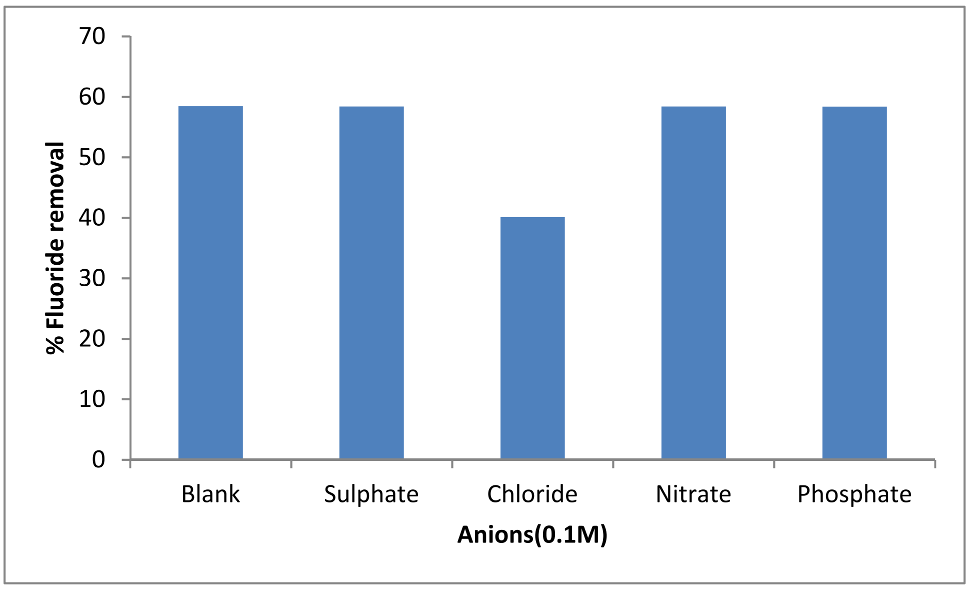

Figure 18 Effect of co-ions on fluoride ion adsorption

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusions

Acid modification was increased fluoride adsorption capacity of spent diatomaceous earth. Adsorption parameters (pH, initial fluoride concentration, adsorbent and contact time) were investigated using batch method .Maximum fluoride removal was obtained at PH 2.For a given initial fluoride concentration, the fluoride removal efficiency of the adsorbent increased with increasing adsorbent dose. Adsorption of fluoride is very rapid in the first 180min. Initial concentrations of fluoride were found to affect the defluoridation efficiency of the adsorbent.

Response surface methodology by the Box–Behnken model was used to examine the role of four process factors on fluoride removal. It was shown that a second-order polynomial regression model could properly interpret the experimental data with coefficient of determination (R^2) value of 0.9949 with F value of 196.55. The simultaneous optimization of the multi-response system by desirability unction indicated that 42.94% removal of fluoride is possible using ATSDE. The Langmuir and Freundlich adsorption isotherm described the experimental results and maximum adsorption capacities; q_{max} of the adsorbent was 0.321mg/g. Acid treated spent diatomaceous earth could be used as adsorbent for fluoride ion containing aqueous solution

5.2. Recommendations

In this study the particle size of the spent diatomaceous earth is not taken into account. The relation between the particle size and its affinity to adsorb fluoride should be studied as well. The column experiments and regeneration procedure should be studied further

Previous study showed that treatment of clay adsorbents by chemicals such as Aluminum and Iron gave better fluoride adsorption capacity .To exploit this effect further study should be conducted on chemical treatment using the aforementioned chemicals and others.

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