FLUORIDE REMOVAL BY CITRUS LIMETTA PULP AND CITRUS SINENSIS PEEL USING BATCH PROCESS: KINETICS AND EQUILIBRIUM STUDIES

Thesis submitted in partial fulfillment of the requirements for the degree of

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By

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This is to certify that the thesis entitled, "**Fluoride Removal By Citrus Limetta Pulp And Citrus Sinesis Peel Using Batch Process: Kinetics and Equilibrium studies"** submitted by Mr. JITENDRA KUMAR in partial requirements for the award of Master of Technology Degree at the Delhi Technological University, Delhi is an authentic work carried out by him under my supervision and guidance.

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This thesis is the account of six months of devoted work in the field of Environmental Engineering at the Delhi Technological University, Delhi, India, which would not have been possible without the help of many.

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DECLARATION

I, hereby declare that the work being presented in the Project Report entitled "**Fluoride Removal By Citrus Limetta Pulp And Citrus Sinesis Peel Using Batch Process: Kinetics and Equilibrium studies"**is my original work and an authentic report carried out during the period of 4thSemester as a part of my major project.

The contents of this report has not been previously formed the basis or the award of any degree, diploma or other similar title or recognition and is being utilized by me for the submission of my Major Project Report to complete the requirements of Master's Degree of Examination in Environmental Engineering, as per Delhi Technological University curriculum.

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ABSTRACT

In the present study removal of fluoride from synthetic water using citrus limetta (mosambi) fruit pulp powder and citrus Sinensis (Malta fruit) peel powder has been carried out through batch adsorption process. The effect of various parameters like pH, agitation time and initial fluoride concentration was studied. In case of both the materials maximum removal of fluoride is observed at pH 7. Test was also done at pH 5 and 9. In case of mosambi pulp equilibrium time has been found around 45 minutes whereas in case of Malta peel powder it was found to be around 60 minutes. At this point graph becomes almost parallel to x-axis which shows that there is no further effect of time on removal of fluoride. Initial fluoride concentration graph was found to be almost linear. It is plotted between initial concentration of fluoride and adsorption capacities at equilibrium “qe” (mg/g). To understand the phenomenon of adsorption kinetic models and equilibrium models has been applied and there constants and various parameters were also calculated. Various models applied were Langmuir, Freundlich, temkin (equilibrium models) and pseudo-first order, pseudo-second order, intra particle diffusion, Elovich model (kinetic models). In case of mosambi pulp powder Langmuir adsorption isotherm has maximum value of R^2 i.e. 0.7991 hence this model fitted well among all equilibrium models and among kinetic models the adsorption kinetics is well presented by the pseudo-first order rate equation which has maximum R^2 value i.e. 1. In case of Malta fruit peel powder temkin adsorption isotherm has maximum value of R^2 i.e. 0.9869 hence this model fitted well among all equilibrium models and among kinetic models fluoride adsorption is well explained by Elovich model which has maximum R^2 value i.e. 0.9890. There are many industries which use fluoride in production and industrial applications, such as semiconductors, fertilizers, and electrolysis of alumina; hence they contribute to fluoride pollution. Concentration of fluoride determines whether it will be harmful or beneficial in the drinking water. It has been proved that fluoride concentrations between 0.5–1.5 mg/L are beneficial especially for newborns because they prevent dental caries and tooth decay, whereas concentrations more than 1.5 mg/L cause mottling of teeth in mild cases but fluorosis (dental or skeletal) and several neurological disorders in severe cases. Therefore various methods and materials need to be find out which shall be economical and highly efficient in Deflouridation process. Cost is one of the important factor hence more number of low cost adsorbents should be developed.

Key words: citrus limetta, citrus sinensis, fluoride, kinetic models, equilibrium models.

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Chapter 1

INTRODUCTION

Now it is a well-known fact that Fluoride leads to health hazards which includes grave environmental problem across the world. Both natural as well as anthropogenic activities are responsible for this problem. As we know fluoride is found in various naturally present deposited minerals as well as geological deposits, it can percolate into the ground with rainwater, hence polluting both surface and ground water [1]. There are many industries which use fluoride in production and industrial applications, like semiconductors and alumina electrolysis; therefore creating fluoride pollution. levels of fluoride determines whether it will be harmful or beneficial in the drinking water. It has been proved that concentration of 0.5–1.5 mg/L proved beneficial for newborns because they prevent dental caries, decay of teeth , but if the fluoride level is more than 1.5mg/l than it will cause other problems like teeth mottling when condition is mild and disease of nervous system in serious cases.

The fluoride level in groundwater in many parts around the world exceeds the permissible limits. Fluoride is released from various engineering processsuch as thermal power plants, production of ceramic and glass, uranium purification, fertilizer production, rubber production and semiconductor manufacturing and natural sources. Therefore higher concentration of fluoride should be removed from water[4,5].

Various methods have come up for fluoride removal but most of them are not suitable for developing countries like India. some of the methods are electrochemical, coagulation and also ion exchange, use of membrane. Research of Ayoob et al.[6]and Mohapatra et al.[7] have given effective techniques for the removal of fluoride. Among these techniques adsorption is very economical. It also proved effective and environment friendly . Different adsorbents for defluoridation have been testedlike activated alumina,[8-9] kaolinite,synthetic resins, carbon nanotubes, bone char, manganese oxide-coated alumina, double layered hydroxides, [10] etc. Activated alumina is one of the adsorbent widely used in removal of fluoride from water, but it is most effective at low pH. Lot of research have been done for the removal of fluoride but in most of the cases adsorption of fluoride is not satisfactory [11]. Many techniques have come up in recent years, to develop new and cost-effective fluoride adsorbents. India being a developed country is trying to find a material which is cheap and easily available. Fluoride is found in many parts of India and the world.

1.1 Occurrence of fluoride in the environment

Fluorine is the halogen member which is considered lightest among the group and it is very reactive in nature in all elements. hence it is found in different foams but not as fluorine in nature. It is the highest of all electronegative elements which indicates its strong affinityfor acquiring negative charge, and found as F– ions foam in the solution. It has also been observed Fluoride ions has same chargeand radius like hydroxide ions and can replace oneanother in structures. Fluoride generally will form complexes with the Cations andcommon compounds of low solubility having fluoride. Hence in environment it is found in the foam of fluorides,it isaround 0.06–0.08% of earth crust. It is found that the average abundance of crust is 300 mg/ kg. Fluorideisreported in significant amount in various mineralssuch as fluorspar,rock phosphate, cryolite, mica, hornblendeand apatite. Fluorite is found as a wide fluoride compoundhaving low solubility found in both sedimentary rocks as well as igneous rock. It is because of volcanic activity as well as fumarolic in gaseous foam.Thermal waters having higher pH are rich in theconcentration of fluoride. Minerals having commercial significanceare rock phosphatesandcryolite.

1.1.1 Distribution of fluoride in water

Now it is a well-known fact that Fluoride occurs in different natural waters having various concentration. Seawater have around 1.1mg/ l and river, lakes have level of fluoride lower than 0.6 mg/ l. groundwater’s can have low and high level of fluoride which depends on the various type of rocks and also occurrence of fluoride having minerals. concentration of fluoride in the water is limited depending upon fluorite solubility, hence in presence of 39 mg/ l concentration of calcium it is only upto 3.2 mg /l. if the calcium is absent then only higher level is found to be stable. Higher fluoride amount may be there in the groundwater source from the low calcium aquifers and can be in the areas where minerals having fluoride are common.

Level of fluoride may increase in ground waters in which exchange of cation of Sodium in replacement of calcium ion occurs. Fluorosis is described as serious disease in most tropical climates, but this does not the happen. Waters with high level of fluoride amount can occur generally in wide geographical area link with a) sediments which have marine origin in regionof mountains, b) volcanic rocks, c) gneissic and granitic rocks. It's example can be taken starting from counties like Iraq and Syria going through Iran and then Turkey to sea of Mediterranean, and including Algeria and the Morocco. Other important examples can be taken from the southern parts such as southern Europe and USA and then region of the USSR. High sub surface water fluoride concentrations linked with rocks like igneous and metamorphic has been foundin India, Thailand, Pakistan,Sri Lanka, and South Africa.

In China high fluoride level have been found in all twenty ninestates,in different Areas and municipalities region accept Shanghai. Upper level and low depth both water are having high fluoride levels but mostly deeper ground water havefluoride concentrations at higher side. In Srilanka concentrations of range 10 mg /l in ground water in Dry Zonecauses dental and also skeletal fluorosis. In Wet Zone having high rainfall higher leaching and minerals compounds from rock like crystalline might be responsible for less concentration.

Efforts for solution of fluoride in drinking water supplies in countries like India is doneby Rajiv Gandhi National Drinking Water Mission, which is having support of other organization such as UNICEF. Despite this it is a big problem in India mostly in rural areas. It is never easy to arrive at the conclusion of estimation people who are at the risk. Its main reason is mainly the difficulty in sampling ground water in Indiafrom millions hand pumps. At Present samplings is done selective but it is also unstructured, taking into consideration only few areas from districts and few pumps from each village leaving the rest. It has come to the report that there has been no detailed health survey to get the information of dental fluorosis so that overall quantity of the problem can be known. However in various affected areas mentioned above, some or more regionhave some villages with groundwater having high level of fluoride. However these states have 11 to 24 % of backward regionwhich is estimated at higher risk and in india total of 70–80 million people might be affected.

1.2 Exposure of fluoride

Fluoride is present in air and also in dental products in some regions. Limit may change depending on the various factors like use of fertilizers and industries in that area.

1.2.1 Air

Because of dust as a result of industrial production of various fertilizers such as phosphate fertilizers and fly ash from burning of coal in the thermal power plants and also due to volcanic activity concentration of fluorideis uniformly distributed in and around the atmosphere. In exposure of fluoride air is responsible only for a very small fraction of amount. However in non-industrial area the level of fluoride in the atmosphere is quite low (0.06–1.80 microgram m–3 fluoride). In the regions where fluoride having coal products burnt and phosphate fertilizers are produced and used.it is reported that fluoride concentration in atmosphere has increased leading to exposure through inhalation route.

1.2.2 Dental products

Various items which are used to reduce the tooth decay by small children contain fluoride. These include toothpaste having 1.10–1.6 gram/ kg fluoride, solutions of fluoride and gels used for the treatment 0.23–25.0 gram/ kg fluoride and fluoride tablets 0.25, 0.61 and 1.2 milligram fluoride tablet each. All the Above products give contribution in the fluoride but to different degrees. It is found that some children swallow the paste having fluoride that might contribute 0.62 or 0.78 mg of fluoride per child/ day.

1.3 Guidelines and standards

WHO had conducted a thorough survey and reported that data collected were insufficient to reach a conclusion that implies fluoride leads to disease like cancer and may cause birth defects. In addition to this WHO concluded mottling of teeth known as dental fluorosis is related with level of fluoride in drinking water more than 1.5 mg/ l and further skeletal fluorosis may occur if level of fluoride increases higher than 10 mg/ l. A value of around 1.5 mg/ l was then recommended by WHO at this level dental fluorosis will be at the minimum degree. The 1.5 mg/ l fluoride levelwhich was fixed in 1984 was revised by the WHO and concluded that there was reported no cases, it was revised. hencethe value 1.5 mg/ l given by WHO cannot be taken as fixed data and can be adapted in different conditions like consumption of water, diet.

It is necessary to consider the consumption of water, weather conditions and certain other critical factors while setting standards in case of concentration of fluoride. These various factors are vital not only in setting national guideline standards for fluoride, but also while taking the standards from one area of the world to different regions where conditions are changing in rest to other region. Hence effects of fluoride can be suitably predicted from its dose in milligram of fluoride per kilogram of weight of body per day and the exposure duration and various other parameters such as age and dental fluorosis. Therefore epidemiological studyrelatedto the negative effects on the teeth of fluoride and also onthe bone has linked the effects with concentration of fluoride in water taken in place of total fluoride exposure.

1.3.1 Indian data on dental and skeletal fluorosis

It is necessary to release the guidelines for the substance which could affect the human health at certain amount of concentration. There are national and international guidelines which need to be followed. Situation of a particular country needs to be understood before carrying out any scientific study.

Fluoride related health effects

It is found that out of 32 seventeen States are suffering from the endemic fluorosis in various regions of India (Yadav *et al*. FRRDF, 1999,). In the year 1987, it was also found that 25% million people were affected from the condition of fluorosis (FRRDF, 1999).

Fluorosis, exposure and fluoride concentrations

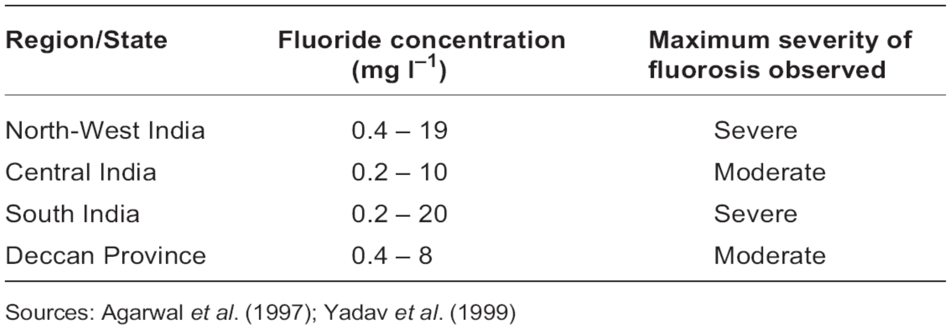
17 States are affected by the increasing concentration of fluoride in water, these are, Assam, Bihar, Delhi, Haryana,Andhra Pradesh Jammu and Kashmir, , Gujarat,

Kerala,Karnataka Madhya Pradesh, , Maharashtra, Orissa Punjab, , Rajasthan, UP,Tamilnadu, and west Bengal.

All the above states reportedfrom long time identified by the very first report (Short *et al*. (1937) among all Assam is the most recently identifyregion with highestlevel of fluoride related with fluorosis endemic. all the above regions are not affected equally and number may vary in different districts with the condition of endemic fluorosis. Nine out of eighteen districts in the state West Bengal identified having fluoride in groundwater (Ministry Water Resources 2004). It has been found over 66 million people of total population are affected by fluorosis. This number is increasing day by day.

It is reported that Instate like Rajasthan fluoride levelmay vary from 0.5 mg/ litre and 69.9 mg/ litre. However in Haryana 48 mg/litre was the highest concentration reported in the village karoli. It has been reported that fluoride concentration 0.3 and 6.9 mg/litre in jeenddistrict in four villages of HaryanaMeenakshi *et al*. (2004.

Table 1.1: Fluoride concentrations in groundwater of India



Region/State	Fluoride concentration (mg l^{-1})	Maximum severity of fluorosis observed
North-West India	0.4 – 19	Severe
Central India	0.2 – 10	Moderate
South India	0.2 – 20	Severe
Deccan Province	0.4 – 8	Moderate

Sources: Agarwal *et al*. (1997); Yadav *et al*. (1999)

1.4 Aims and Objectives of the Present Investigation

1. To study effectiveness of citrus limetta (mosambi) fruit pulp powder in removal of fluoride at different pH, time and concentration of adsorbent from water.
2. To study effectiveness of citrus Sinensis (Malta fruit) peel powder in removal of fluoride at different pH, Time and concentration of adsorbent from water.
3. To study kinetics models for citrus limetta pulp powder and citrus sinensis peel powder.
4. To study equilibrium models for citrus limetta pulp powder and citrus sinensis peel powder.

Chapter 2

LITERATURE REVIEW

Ikuo Abe et al. (2004) investigated the removal of fluoride onto the carbonaceous materials. It was found that Bone char to be the most effective material. Phosphate ions present in the bone char found to be helpful in the removal of fluoride ions by the ion exchange process. This process was found to be chemical not physical as the removal of fluoride ions enhanced with falling PH and increase in temperature. It was also found that it is a endothermic process in nature during which the heat is absorbed. Deflouridation of Drinking water can be done with the help of bone char [12].

Yunus C et al. (2002) investigatedremoval of fluoride with the original and activated red mud from aqueous solution. Investigators used batch equilibration process. Various parameters like pH, adsorbent dose and contact time were investigated. The fluoride removal adsorption capacity of the activated form shows higher removal capacity than the original form. Experiment shows that fluoride ion removal was maximum at pH 5.5. Research data was fitted with Langmuir and Freundlich isotherms. Study revealed Langmuir adsorption isotherm curve to be more significant. Investigators also determined equilibrium time for fluoride removal which was found to be 120 minutes [13].

SrimanthKagne et al. (2008) studied the potential of bleaching powder for the removal of fluoride from aqueous solution. It was found that adsorbent dose of 50g/L at the PH range of 6-10 was efficient for the removal of fluoride to desired level.Investigators found that Langmuir model fitted well to equilibrium adsorption data. Researchers concluded that fluoride removal was maximum at one hour. They also found the competition for adsorption with fluoride ions. The ions giving competition were sulfate, nitrate and chloride. Study concluded that removal of fluoride was higher in synthetic water in comparison to field water [14].

EnsarOguz (2006) carried out the Equilibrium isotherms and kinetics studies for the sorption of fluoride on light weight concrete materials. Various parameters like PH, agitation rates and temperature of solution were into consideration. Fluoride ions were removed from synthetic solution using pseudo-second order kinetic model. He used jar test for finding the equilibrium time which came out to be one hour. Optimum values of K ads gmg−1 min−1 at different parameters like pH (6.9), temperature (333K) and agitation rate (235 rpm) were found to be 0.300, 0.225 and 0.147 respectively. He found the mean energy of sorption as 8.68 kJ mol−1 with the help of D-R sorption isotherm [15].

Wan-Hyup Kang, Eun-I Kim, Joo-Yang Park (2005) investigated Fluoride removal capacity of cement paste. Three Ca-bearing materials cement, cement paste and lime were tested. Cement paste was found to be more effective in removal of fluoride. Researchers concluded Cement paste contains Ca-bearing hydrates like portlandite, calcium silicate hydrate (CSH), and ettringite they were responsible for removing fluoride by either precipitating CaF2 or adsorbing F– ions. Both batch slurry and column process were done. In batch slurry 50-67% lime was replaced by cement paste. It was also found that PH affected the fluoride removal in batch slurry experiment. An optimum PH of about 7 and 11.5 existed. From the column experiment it was found that an initial concentration of the real hydrofluoric acid wastewater of 1150 mg/L came down to less than 15 mg/l in the column effluent [16].

Nan Chen et al. (2010) studiedFluoride removal from water by developing a new material granular ceramic**.** It removes fluoride by adsorption process. This newly developed material is a solid –phase medium which produces a stable Al–Fe surface complex for fluoride adsorption. Batch process was used to study different parameters. It was found that Maximum removal of fluoride was obtained from pH 5.0 to 8.0. Three temperatures 293, 303 and 323 K were set to obtain equilibrium adsorption data at all three temperatures. Data was analyzed using Langmuir and Freundlich isotherm equations. The experimental data shows that the Freundlich isotherm equation was fitted well for fluoride removal in comparison to Langmuir isotherm. Pseudo-second-order kinetic model was found to be followed by the adsorption process. It was revealed that phosphate and sulfate ions reduce the adsorption of fluoride ions whereas it was increased slightly in the presence of chloride and nitrate ions [17].

Ali Tor (2006) studied Removal of fluoride from an aqueous solution by using montmorillonite. Batch adsorption process was used for the experiment. Maximum efficiency of fluoride removal was found at the PH 6. Experiment determined the equilibrium time for removal of fluoride as 3 hours. He also analyzed best-fitting adsorption isotherm which was found to be Freundlich isotherm. It was observed that fluoride saturation capacity of montmorillonite is 0.263 mg/g at room temperature. Adsorption isotherms were well determined by the non-linear Chi-square statistic. He also carriedout desorption studies which show that fluoride can be easily desorbed at PH 12 and adsorbent can be recycled. It was also found that efficiency decreased from 65 to 58% after the first regeneration when the initial fluoride concentration was 4mg/L [18].

A. Teutli-Sequeiraet al. (2013) studied Comparison of aluminum modified natural materials in the removal of fluoride ions. Three materials used were aluminum modified hematite, zeolitic tuff and calcite to study the fluoride removal from aqueous solutions and drinking water. It was found that aluminum modified zeolite having adsorbent dose of 10 g/L with an initial fluoride concentration of 9 and 8.29 mg/L for the aqueous solutions and drinking water respectively was most effective. Also equilibrium data fitted well to Langmuir–Freundlich isotherm model whereas Adsorption kinetic data were best fitted to pseudo-second-order and Elovich models. Data fitting to kinetic and isotherm models shows that main mechanism attributed in the adsorption of fluoride ions is chemisorption onto the heterogeneous materials [19].

Nan Chen, Zhenya Zhang et al. (2010) have doneInvestigations on the batch and fixed-bed column performance of fluoride adsorption by Kanuma mud. Batch study shows that maximum fluoride removal was achieved from pH range 5.0 to 7.0, which took around 120 minutes to achieve equilibrium. It was found that Equilibration time was independent of the initial fluoride concentration. It was observed that Kinetics data were fitted well to the pseudo-second-order model and experimental data fitted well to a Freundlich adsorption isotherm. Different parameters like different influent fluoride concentrations, bed depths, and various flow rates were taken in the Fixed-bed column experiments. They applied two models bed depth service time model and the Thomas model to the experimental results. Investigators found both model predicted well in agreement with the experimental data for the different parameters taken into consideration suggesting that the models were suitable for Kanuma mud fix-bed column design. Desorption of column was done by pumping 0.1 M NaOH in the loaded Kanuma mud column [20].

Noureddine Hamdi, Ezzeddine Srasra (2006) investigated Removal of fluoride from acidic wastewater by clay mineral. The efficiency of H, MK and ZB three Tunisian clay was determined in the experiment. Different parameters studied were solid–liquid percentage (10, 20 and 30%), contact time, PH and effect of concentrations of other ions. It was observed that agitation increases the efficiency of fluoride removal. The equilibrium was achieved within 48 h time lowest and the highest adsorption was reached for MK clay for clay–lixiviat suspension of 10%. Langmuir isotherm model fitted well for all samples. It was also found that effect of other ions on fluoride removal depends of the relative affinity of the ions by the type of clays and also on the relative concentrations of ions [21].

A. Ramdani et al. (2009) studied Removal of excess fluoride ions from Saharan brackish water by adsorption on natural material by retention process onto montmorillonite clay using potentiometric method. They tested two types of natural clays one which have a higher percentage of calcium (AC) and the second without calcium (ANC). They activated the clay chemically and thermally in the temperatures range between 200 and 500 degree Celsius. Chemical activation provided greater efficiency in the removal of fluoride in comparison to the thermal activation with adsorption reaching up to 88% and 5% respectively. Adsorption isotherms were found to be well fitted with Langmuir's model. It was observed that process was exothermic [22].

J.J. García-Sánchez et al. (2013) investigated Removal of fluoride ions from drinking water and fluoride solutions by aluminum modified iron oxides in a column system. They draw breakthrough curves for fluoride ions adsorption from aqueous solutions and drinking water and fitted well to Thomas, Bohart–Adams, and bed depth service time model (BDST). Adsorption efficiency at breakthroughs and Thomas model constant, kinetic constant and also the saturation concentration were obtained. It was reported that the adsorption efficiency decreases as the bed depth increases which demonstrate that the adsorption is controlled by the mass transport resistance. Experiment shows that adsorption efficiency for fluoride ions by CP-Al was found to be higher for fluoride aqueous solutions than drinking water [23].

Mitali Sarkar et al. (2006)studied Use of laterite for the removal of fluoride from contaminated drinking water. Initial fluoride concentration, agitation time and speed, dose and particle size of laterite, solution pH, and temperature were the parameters which were taken into consideration. It was reported that fluoride removal was maximum at lower concentration, smaller particle size of laterite, increased agitation time and speed, increased dose of laterite, and lower temperature. Both Langmuir and Freundlich isotherm model were in agreement with the equilibrium data. They found that column operation was affected by the feed fluoride concentration, pH, flow rate, and column bed height. The bed depth–service time model was made to predict fluoride removal corresponding to a certain bed height. They came to the conclusion that use of laterite as an adsorbent for fluoride removal is cost effective [24].

Rahul Trikha ,BalKrishan Sharma (2013) studied different factors affecting fluoride removal from water using passive system. Reverse osmosis, batch experiment column experiment were conducted to determine the effects. AR grade chemicals were used in the experiment. CaCO3 with purity more than 98% was used as adsorbent. They used HF, MgCl2, CaCl2, NaNO3, Na2SO4, chemicals (AR grade) for simulating feed water. They found that PH range 6 to 7 was effective in the removal of fluoride. Maximum value of removal was reported at 30 degree Celsius temperature. The column experiment shows that it is an economical method, which does not require additional treatments or equipment like RO [25].

H. Lounici et al. (1997) studied a new technique which was based on the combination of an activated alumina column and an electrochemical system for fluoride removal from water. Initially the optimization of the process was done under various experimental parameters such as, temperature, pH, volumetric flow initial fluoride concentration and hardness with a synthetic solution. It was found that adsorption capacity of the activated alumina column reached 3.8mg F-/L at the breakthrough point. It was increased to60% by electrochemical process in comparison to current mode result. They reported that saturated activated alumina can be regenerated by electro sorption system. Hence it was concluded that the electro sorption process combine with activated alumina column was successfully applied for the removal of fluoride from drinking water [26].

AyseDilekAtasoy et al. (2013) studied In this study, serious fluorosis cases were identify in the primary school in Sarım and the Karataş village located in north west in the Şanlıurfa in Turkey . There fluoride levels in the water in those village were identify in 2011. From Results of experiment concluded that the fluoride levels in the water samples were more than the national and international guideline limit values for ground water (more than 1.5 mg/ L). Therefore fluoride levels in drinking water must be decreased to an permissible level that was prescribed in Turkish Standards of water. It was decided to introduce a new high-fluoride serious problem in all different parts of Turkey which was not identify in " Water Fluoride Map of turkey" and to find the removal of fluoride possibilities from the drinking water by adsorption on activated carbon for an quick solution.The Commercial activated carbon was utilized as the adsorbent in the Fluoride adsorption study. The maximum adsorption rate of Fluoride onto the activated carbon was found to as 50 percent. Freundlich equation were well fitted to the Fluoride adsorption. But fluoride adsorption onto the activated carbon was observed lower with the Kf value of 0.056[27].

K.A.Emmanuel et al. (2008), The study have also been conducted on removal of fluoride on commercial activated carbon (CAC) and the indigenously prepared activated carbons from Ipomoea batatas, Pithacelobiumdulce, and Peltophorum ferrugineum have been done. The effects of different experimental parameters such as pH, adsorbate concentration , dose of the adsorbent and the contact time have been find out using the batch adsorption method. The extent of removal of fluoride got increased with the decrease in initial concentration of fluoride and the size of particle of the adsorbent and also got increased by increase with the amount of adsorbent used, the contact time and with the initial pH of the solution. Adsorption data were put into the Freundlich and Langmuir adsorption isotherms, they followed the first order kinetic equation of equation –dF/dt= Kr (F). The experiment data obtained give a straight line fitted well with a relatively well correlation coefficient (R^2) showing the acceptability nature of the model for the investigated indigenously prepared activated carbons in the fluoride system. R^2 values of PLDC was0.09967, IBC came out to be 0.9953, PFC= 0.9946 and the CAC was 0.9946]. The kinetics was found as first ordered with intra particle rate of diffusion. The results of the experiments data have proven that the percentage of fluoride removal has got increased with increase in contact time and also with the dose of adsorbent. On the other hand the percentage removal of fluoride got decreased with the increase in the initial concentration of standard solution of fluoride. The results have shown that intra particle adsorption was very important process in adsorption. The adsorption process is observed to be first order including intra particle diffusion one of the most important rates determining process. Among all the adsorbents that were considered PLDC have the highest and the maximum adsorption efficiency. [28].

Sushree Swarupa Tripathy et al. (2006) have done study on capacity of the alum impregnated activated alumina for the removal of fluoride from drinking water by adsorption has been done in the present study. All the investigation is carried by batch process. The effect of various parameters like contact time, adsorbent dose (0.5–16 g/l), pH effect (2–8), initial fluoride concentration (1–35 mg/l) has been study to know the adsorption efficiency of AIAA. The isotherm data and adsorbent dose are correlated to the equation Bradley. The efficiency of the AIAA for removal of fluoride from drinking water is found to be 99 percent at the pH 6.5, dose of 8 g/l, contact time for 3 h, when around 20 mg/l of fluoride concentration is present in about 50 ml of water. Energy dispersive experiment of X ray demonstrates that the consumption of the fluoride at the AIAA and interface of water is because of surface precipitation. The desorption experiment shows that the above adsorbent can be easily regenerated by a simple base acid rinse procedure but further impregnation of the recovered adsorbent is required for further removal of fluoride process[29].

S. T. Ramesh et al. (2012), in this particular study adsorption capacity of bottom ash was determined for removal of fluoride in the drinking water using continuous fixed bed column experiment and batch. Batch adsorption fluoride removal conducted by experimental parameters such as pH, agitation time , temperature, the particle size and dose. Adsorption isotherms used were Langmuir and Freundlich isotherms. The fluoride adsorption efficiency at the point of breakthrough for the bottom ash was particularly influenced by the bed depth. The results were investigated using Bed Depth Service Time Model, and different performance parameters such as Adsorption efficiency, Adsorption Rate Constant and Critical Bed Depth were find out. With the experiment data the Yoon Nelson model and Thomas model were well fitted and the constants were determined.The optimum contact time for Deflouridation was determined to be 105 min with the maximum capacity of 73.5 percent at 70mg per100ml bottom ash dose. The optimum pH came out to be pH of 6 with the maximum capacity of 83.2 percent. Further the removal of fluoride got increased with the decrease in the size of particle. The highest monolayer adsorption efficiency of bottom ash was observed to be 16.26 mg per g at the 303 Kelvin. From the study of column it wasdetermined that the increase in fluoride ion consumption due to increase in the bed height was because of increase in the time of contact. [30].

N. Gupta et al. (2014) found Excessive fluoride levels in ground waters of regions of more than 20 developed and the developing countries involving India where more than 19 states are reported to have acute fluorosis. This present experiment was done for the determination of fluoride in drinking water in the city of Agra's urban and rural parts. Batch tests were conducted on water samples from the different parts at St. John's College Chemistry Department, in tha area of Gokulpura, Trans Yamuna, and Dareshi that have 2.0, 3.5, 2.5 and 4.2 mg per litre of fluoride respectively were done using bagasse flyash (BF), bagasse dust, aluminium treated bagasse flyash, buffalo bone powder (BP), clam shell powder . The different tests were also conducted with 3.8, 1.9, 9.5 and 4.75 mg/litre NaF solutions. The work was aimed to determine the feasibility of using biomaterials for the fluoride ions removal from the groundwater so that it can be fit for drinking and industrial use. Fluoride removal was in the ranking of SP > BP > ABF > BF > BD on the wide initial concentration of 1-10 mg per litre at adsorbent dose range of 1-20 g per liter at pH 6.0, rpm 150, temperature 25°C for 5 hour tome. The adsorption rate increased with increasing time of contact and adsorbent dose but the equilibrium was achieved only after 4 h for most of the adsorbents. Groundwater samples were observed to be 2 to 10% lower removal of fluoride as compared to standard sodium fluoride solutions under same conditions. It was observed that clam shell was the best of all the Deflouridation agents studied [31].

Kaushik Bandyopadhyay et al. (2009) have done study on broken cubes of concrete generated from different construction projects which we all know are a major cause of concern with respect to its safe disposal. In view of this it considered best to utilize them for removal of fluoride present in groundwater. This present research reports an experiment on the removal efficiency of broken cubes of concrete for the removal of excess content of fluoride from aqueous solution using column adsorption process. Synthetic fluoride solution was utilized for this process. The influence of various adsorption parameters like initial concentration, effect of adsorbent dose, contact time and PH was done for their optimization content determination. Percentage removals of fluoride as a function of time period and uptake efficiency related to volume of flow were determined by analyzing the different breakthrough curves. Finally, it was noticed that broken cubes of concrete are effective in removing fluoride content from groundwater source. It was found thatBroken cubes are most suitable adsorbent for fluoride removal from drinking water. The broken cube was determined to reduce about 80 percent fluoride at 120 minutes of contact time. Removal fluoride percentage by broken cube was observed to increase with the increase in adsorbent dosage.Broken cube would remove sufficient level of fluoride over a wide range of pH. Maximum removal was done at pH 7. The removal of fluoride from water of the field investigated area was more than satisfactory[32].

R. Bhaumik et al. (2012) have done study on a new material powder of eggshell for fluoride removal from the aqueous solution having fluoride. Fluoride adsorption was done in a batch process where adsorption was determined to be pH dependent with highest removal capacity at 6.0. The research data was more suitably fitted with the Langmuir isotherm model. Whereas kinetics and the controlling adsorption system fully accepted in the pseudo second order model were discussed. Ea was determined to be 45.98 kJ/mol by use of Arrhenius equation showing chemisorption nature of fluoride process on the eggshell powder. Thermodynamic experiment showed spontaneous nature of process and feasibility of adsorption process system with negative enthalpy value also suggested theexothermic nature of reaction. Batch study were done to study the suitability of the adsorbent by the use of fluoride contaminated drinking water taken from affected areas. These results show that eggshell powder may be used as an suitable, low cost adsorbent for removal of fluoride from aqueous solution and also from groundwater[33].

Waheed S. Deshmukh et al. (2009) undertook batch adsorption experiment to determine the suitability of low cost adsorbent prepared from the agricultural waste like rice husk. The adsorbent was prepared by the use of chemical impregnation process followed by physically activating it. Static experiment have been done for investigation of fluoride removal capacity under the different conditions of the major various parameters of adsorption like dose of adsorbent, pH, rate of stirring initial adsorbate concentration and contact time and analyzed by batch process in the mixture of known levels of fluoride solution. The optimum adsorbent dose was determined to be *10g per L* by changing the dose of adsorbent between 0 to *16 per L during this process* equilibrium was achieved in 2 hours at the optimum pH. It has been noticed that the optimum adsorption of fluoride takes place at lower pH by changing pH from 2 to 10. Maximum removal of fluoride was found to be 75 percent at optimum conditions. Freundlich and Langmuir isotherms were plotted to determined constants of isotherms[34].

Yi Zhang et al. (2013) have done study on a new adsorbent which is bentonite and chitosan beads has been developedand investigated for its defluoridation capacity. Bentonite has been activated and the beads were manufactured by using the inverse suspension polymerization method. The bentonite and chitosan beads (bentonite dose of 3.0 gram) showed an adsorption efficiency of 0.895 mg per gram whereas chitosan beads was found to have only 0.359 mg per gram. The optimal pH value was noticed at pH 5 where the adsorbent attained the maximum defluoridation efficiency of 1.164 mg per gram. The effect of contact time, temperature , and initial fluoride level on the adsorption efficiency of the adsorbent has also been done. energy dispersive X-ray analysis, Scanning electron microscopy and Fourier-transform infrared spectrometry (FTIR) were used to characterize the properties of adsorbent. The adsorption of fluoride on the adsorbent well fitted Freundlich isotherm model and also pseudo second order kinetic model. The fluoride adsorbent could be reproduced using sodium hydroxide [35].

Xiaoli Zhao et al. (2010) have done study on the magnetic which is nano sized adsorbent was prepared using hydrous aluminum oxide combine with Fe3O4 nanoparticle and was applied to remove excessive fluoride level from the aqueous solution. This adsorbent gives the advantages of magnetic size nanoparticle and also hydrous aluminum oxide floc with themagnetic separation capacity and high affinity for fluoride, which gives different merits including easy manufacturing, high adsorption efficiency, easyseperation from the sample solutions by the use of an external magnetic field atmosphere. The adsorption efficiency calculated by Langmuir isotherm was 88.48mg/g at a pH of 6.5. Main parameters affecting the fluoride removal such as pH of solution, it's temperature, time of adsorption, initial concentration and also coexisting ions were studied. The adsorption efficiency increased with the temperature and it was observed that kinetics follow pseudo second order equation. The enthalpy change and the entropy change was found to be 6.836 kJ/ mol and 41.65 J/ mol/, which concludes the spontaneous nature and endothermic nature of the fluoride removal process. Further the residual level of fluoride using the Fe3O4Al(OH)3 NP as the adsorbent can reach 0.3mg/Liter with the initial level of 20mg/Liter which satisfied the standard of World Health Organization guidelines for drinking water standards. All the results shows that the Fe3O4Al(OH)3 NP having very strong and specific affinity for fluoride can be good adsorbents for fluoride removal in the water treatment process[36].

Jadhav A S, Jadhav M V (2014) In the present experiment batch adsorption method was conducted to investigate the capacity of Maize husk fly ash as an adsorbent for fluoride removal from drinking water. During the research work, effects of various important parameters of adsorption, like Ph, Contact time, Adsorbent dosage and rate of Stirring on removal capacity were done and optimized. Freudlich, Temkin, Langmuir,andRedlich-Perterson isotherms models have been plotted and well fitted model was found.For the parameter of contact time, equilibrium was reached at 2 hours.equilibrium was reached for pH value at 2. The percentage of defluoridation was observed to be a function of time of contact and adsorbent dose at the given initial fluoride level. In case of factor of adsorbent dosage, equilibrium of 2 gram was obtained. Whereas the maximum capacity was found to be 86 percent. For Stirring rate parameter change, the equilibrium of stirring at rate of 250 revolution per minute was found. The maximum capacity of adsorption was found to be 84.71% percent for maize husk fly ash. As for maize husk fly ash, the removal of fluoride increased with increase in time stirring rate and adsorbent dose but for varying the value of pH and the removal capacity got decreased with increased value of pH. The last phase of the investigation validated the results came from batch process by using adsorption isotherm models. The present study on removal of fluoride using maize husk fly ash material as adsorbent shows that equilibrium data fitted well to Redlich-Pertersonmodel [37].

Aash Mohammad, CB Majumder investigates the capacity of three low cost bio adsorbents like banana peel, sweet lemon peel and groundnut shell for industrial waste water removal of fluoride at neutral PH value. Efficiency of these different adsorbents on fluoride removal was compared with commercially present adsorbents. It was notice to be better, high removal capacity at high concentration (20 mg per liter) of fluoride in the industrial waste water.Reaction of adsorption kinetics was observed to be pseudo second order and the system of removal of fluoride on adsorbents was notice to be of complex nature. The adsorption on the surface and intra particle diffusion gives to the rate-determining step.The groundnut shell ,banana peel, and sweet lemon peel removed 89.9, 94.34 and 59.59 %respectively from the aqueous solution of concentration 20 mg /l fluoride at different values of pH of 7, 6.0, and 4.0 respectively.Contact time for groundnut shell , banana peel and sweet lemon peel are 75, 60 and 40 minutes and dose 12, 14,and 16 gram/l respectively. reaction of adsorption kinetics was reported pseudo second order reaction, and the method of removal of fluoride on various adsorbents was observed to be complex in nature. The surface adsorption and intra particle diffusion give to the rate determining step. High removal capacity of adsorbent and groundnut shell and banana peel and presence of different ions in water did not considerably affect the fluoride removal process Adsorption isotherm like fruendlich , langmuir and temkin were investigated of these the best adsorption isotherm was Langmuir[38].

N. Gandhi1, D. Sirisha and K.B. Chandra Shekar Fluoride occurs naturally in the water. It is 13 most common element among different compounds of earth crust. Fluoride is very important in preventing tooth decay at very early stages, but when in excess fluoride causes various diseases like Alzheimer diseases , dental fluorosis, skeletal fluorosis, chronic insomnia and thyroid cancer. By investigating the impact of fluoride on human health, low cost deflourination method has been developed. In the present study the batch adsorption experiment are carried out by using waste material like chalk powder. void ratio and Porosity of chalk powder is found to be very high. Due to high porosity of chalk and its chemical composition it is investigated as adsorbent. It is observed that the adsorption process is directly proportional to concentration, contact time and adsorbent dose. The data was investigated into Langmuir and Freundlich adsorption isotherms model. Pseudo first and second order kinetic models illustrate the intensity and efficiency of the adsorbent. The adsorption of fluoride removal by the chalk powder is exothermic and also spontaneous in nature [39].

C.M. Vivek Vardhan1 and J. Karthikeyan (2011) This paper investigates the results of investigations done for removal of Fluoride from drinking water using physic chemical method of adsorption and coagulation using commonly available and low-cost substance such as Rice Husk, extracts of seeds of MoringaOleifera (called Drum stick), and chemicals such as Manganese Sulphate and also Manganese Chloride. Rice husk of 6gram/liter accomplished a removal efficiency about of 83%of Fluoride containing a 5mg per liter of Fluoride solution reaching an equilibrium time of 180 minutes. Equilibrium Isothermal data best suited into rearranged Langmuir adsorption model. Fixed bed down column of flow studies shows the practical use of Rice husk. Standard Jar Tests done with Moringaoleifera seed extracts, Manganese Chloride and Manganese Sulphate got fluorideremoval percentages of 92, 92, 91 and 94 of Fluoride from a 5mgram per liter test solution at a dose of 1000 mgram per liter. the acidic pH of about 6.0 was observe favorable for removal of fluoride by, Manganese Chloride, Manganese sulphate and MOE. The order of reduction in the capacity of anions for Fluoride adsorption is Carbonates > Nitrates > sulphates > chlorides. Influence of ions like sodium and magnesium on the sadorptive removal of Fluoride by Husk is done in this study. The results indicate that ions like sodium and magnesium, have very little influence of adsorptive uptake of Fluoride and the decrease in adsorptive uptake value from 8% to 12%[40].

Bhagyashree M Mamilwar et al. (2012) Presence of Fluoride in drinking water is safe and effective only when it is used as directed, whereas it can be dangerous at high concentration and at low levels. In the present study bark of babool is used as a adsorbent for the removal of fluoride from sub-surface water. Removal of fluoride from groundwater using babool bark as an adsorbent was investigated through the batch process. The effects of various controlling parameters such as contact time , optimum dose , pH and temperature were study. The result concludes that bark of babool of 5 gram per Liter have a removal efficiency of 77.04 percent of Fluoride from a 5mgram per Liter of Fluoride level at pH of 8.0 requiring an time of equilibrium about 8 hours. The research adsorption data were well fitted with Langmuir and Freundlich adsorption isotherms model. The pseudo second-order kinetic model were best suited as compared to pseudo first-order kinetic model. The influence of coexisting ions present in water were also investigated. Comparison was made between simulated water and field water[41].

Y. Hanumantharao et al. (2011) Fluoride is an acute toxic and is considered to be slightly more harmful thanEven to the lead. 48 water samples were collected from different bore wells and hand pumps from 24 gram panchayats of the area of Kanduku sub division of Prakasam district located in Andhra Pradesh and were chemically investigated for fluoride ion levels. Higher and lower fluoride containing areas were identified on the basis of fluoride concentration in the samples of water and also on the basis of dental and skeletal fluorosis of the considered area. hence water samples having high fluoride concentration were tried for removal of fluoride by takingActive Carbons of commonly available low-cost byproducts of plants. These materials studied by taking optimum conditions of time of equilibration, adsorbent dosage and pH were notice to be successfully removing the fluoride ion level below allowable limits without changing other drinking water quality standards[42].

Chapter-3

MATERIALS AND METHOD

3.1 Materials and Methods

Two materials were used for the study of removal of fluoride from the drinking water namely citrus limetta pulp powder and citrus sinensis peel powder.

3.2 Adsorbent collection and preparation

Adsorbent	Sampling Site
Citrus limetta (mosambi) pulp	Raw pulp of citrus limetta were collected from juice vendors of Yamuna vihar and Brijpuri. It was washed dried first in the sun for 2-3 days and then in the oven for 24 hours at about 105-110 degree Celsius temperature. After it got fully dried it was grinded in the grinder to fine powder and finally it was sieved to 425 micron sieve in the soil laboratory of our college. Material was finally ready to be used for the experiment.
Peel of citrus sinensis (malta)	Now the second material fresh malta fruit was collected from the fruit market of bhajanpura. The peels of malta were taken out from the fruit. They were washed and the put into the sun for drying for about 2-3 days. After that dried in the oven for 24 hours at about 105-110 degree Celsius temperature so that no moisture is left in the sample and proper and accurate weighing can be done. Now it was grinded to very fine powder and sieved through 425 micron sieve and sample is ready to be used in the analysis.
 **Fig. 3.1. Peel of citrus sinensis (malta)**	 **Fig. 3.2. Citrus limetta (mosambi) pulp**

3.3 Preparation of Adsorbate Solution

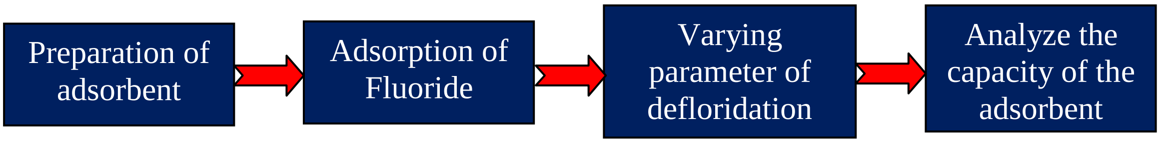
Stock solution was prepared by dissolving 0.22 gm NaF (Sodium flouride) in 1 L distilled water. The required fluoride concentration was prepared by dilution of 100 mg/L fluoride stock solution.

3.4 Apparatus Required

Orion 720 A+ ion analyser was used for finding the concentration of fluoride. The range for caliberation was 0.1 to 10 ppm with the help of known NaF concentration.

3.5 Experimental Procedure

The figure below shows the procedure adopted in the present study.



The study of batch sorption were conducted to know the effect of different parameter like optimum pH contact time, initial concentration. Experiment were conducted at room temperature (29 ± 2°C).

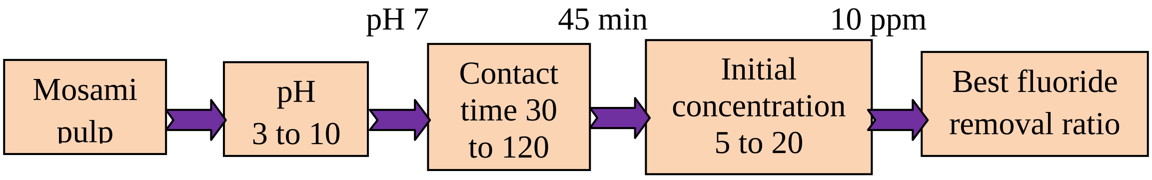


Fig. 3.3 : Experimental programme for Mosami pulp

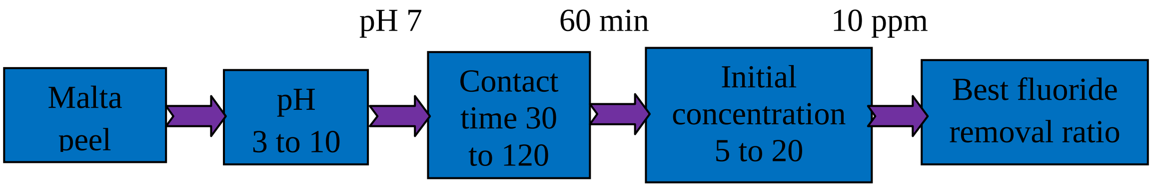


Fig. 3.4 : Experimental programme for Malta peel

3.6 Methodology (Batch Adsorption)

Adsorption experiments were carried out for determination of pH, equilibrium time selection of isotherm.

Different parameter like Influence of pH, contact, time, initial fluoride concentration were evaluated in the present study. Experiments were conducted by adding 10 g/L adsorbent concentration to 500 ml of the test solution in a jar and jar test were performed at an rpm of 125 and fixed time.

Initial concentration of fluoride was taken as 10 mg/L in all cases except where study of initial concentration of fluoride was to be studied. After the jar test. Solution was filtered and collected for analysts of fluoride concentration using ion selective meter. Control experiment was also performed which shows that sorption of fluoride was negligible on walls of jar.

The quantity of fluoride adsorbed per unit adsorbent (q_e) (mg/L) was calculated by following formula

$$q_e = (C_0 - C_e)V/m$$

where V = Volume (L) of the equilibrated solution,

m = Mass of the adsorbent (g)

C_0 = Initial concentration of metal ion (mg/L)

C_e = Equilibrium concentration of Fe^{2+} (mg/L)

The percent removal (%) of fluoride was calculated using the following equation: Removal (%) = (C_0 – C_e/C_0) × 100.

Fig. 3.5 Image of Jar test apparatus used in the study.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Citrus limetta (Mosambi) fruit pulp powder

Effect of pH, fluoride concentration and initial contact time was done on citrus limetta. Different equilibrium and kinetic models was also applied.

4.1.1 Effect of pH on removal of fluoride

Fluoride Removal from drinking water was studied using mosambi pulp at different pH. range. It was found that fluoride removal efficiency got increases upto a value of pH. 7 and then decreases after that value. It was around 45% at pH. of around 5 and maximum was observed at the pH. 7 which was about 75%, at the pH.of 9 removal efficiency was 65%.

Table 4.1: Effect of pH on adsorption of fluoride using Mosambi pulp

pH	Co (initial concentration ppm)	Ce (final concentration ppm)	% removal of fluoride
4.94	10	5.62	43.8
7	10	2.7	73
9	10	3.5	65

Therefore further experiments were performed at the value of Ph7. In this analysis contact time was 60 min and revolutions per minute were 125. Jar test apparatus was used for all the experiments. Samples were prepared and analyzed for final concentration of fluoride.

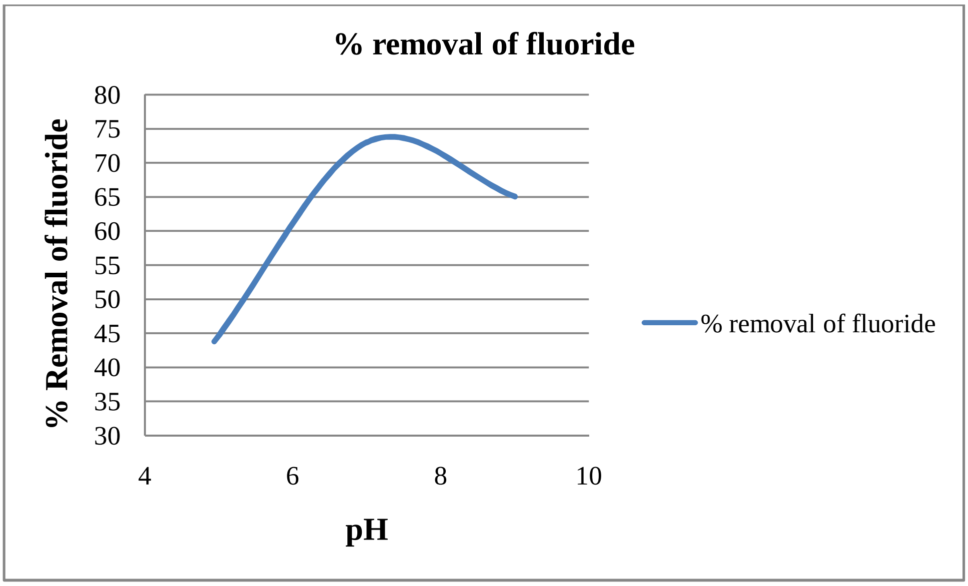


Figure-4.1

pH Effect on removal of fluoride by citrus limetta pulp powder (process conditions: concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, contact time: 60 minutes)

4.1.2 Effect of contact time on percentage removal of fluoride

Effect of contact time was studied and it was found that time of concentration was found to be near about 45 minutes. After 45 min efficiency of fluoride removal was almost constant. The study of contact time was done at pH of 7. It increases from a value of 40 % to 75% at about 50 minutes. Beyond this point it was found that there was no effect of contact time on the removal of fluoride. It was notice that at equilibrium curve is parallel to the x-axis. The change in rate of fluoride removal is because of reason that initially all the surface was available of adsorbent and solute concentration was high. After some time, the fluoride adsorption by adsorbent reduced significantly, due to lesser surface area of adsorbent.

Table 4.2: Effect of contact time on percentage removal of fluoride

Contact time (min)	Co (initial concentration ppm)	Ce (final concentration ppm)	% removal of fluoride
10	10	7.25	27.50
15	10	6.10	39
30	10	4.10	59
45	10	2.72	72.8
60	10	2.70	73
75	10	2.69	73.1

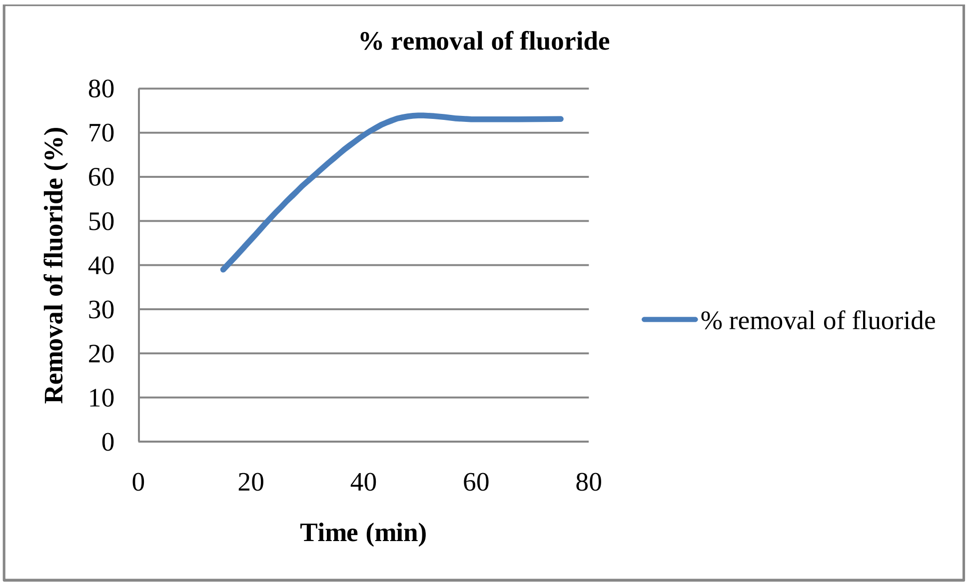


Figure-4.2

Effect of time on removal of fluoride by citrus limetta pulp powder (process conditions: concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, pH: 7)

4.1.3 Effect of initial fluoride concentration

Test was done to know the specific uptake of fluoride by the adsorbent. Concentration of the fluoride was varied from 5mg/l to 20mg/l and it can be seen in the graph that adsorption of ions increases when the fluoride concentration increases. The graph almost followed a linear relationship which shows that adsorption is directly proportional with the value of initial concentration of fluoride. In the ground water value is generally below 5mg/l and at this value final adsorption value was 1.13mg/l which well below 1.5mg/l hence this adsorbent can be very well used for removal fluoride of from water.

Table 4.3: Effect of initial fluoride concentration

Initial fluoride concentration (ppm)	Final fluoride concentration (ppm)	qe
5	1.13	0.387
10	2.72	0.728
15	5	1.0
20	2.76	1.74

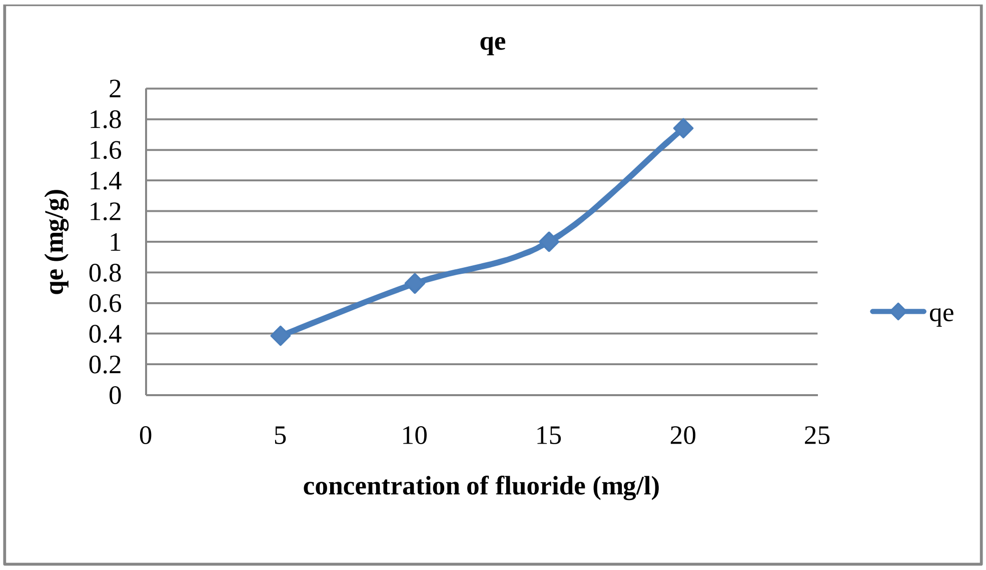


Figure- 4.3

Specific uptake of fluoride by citrus limetta pulp powder (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 45 min)

4.1.4 Langmuir Adsorption Isotherm

The freundlich isotherms model are used only at lower value of temperatures to get the idea about the monolayer coverage and adsorption phenomena of the adsorbent. The Langmuir isotherms model are useful for finding the capacity of adsorbent at higher value of temperature.

Three assumptions :

1. Adsorption can occur only in monolayer coverage
2. All surface is uniform and site are equivalent
3. The molecule can adsorb independently to the site and do not depend on neighboring site

The Langmuir isotherm has linear form as follows

$$1/q_e = 1/a + 1/ab\ c_e$$

Where qe (mg/g) is the ratio of fluoride adsorbed to the dosage of the adsorbent, Ce (mg/l) is the equilibrium concentration of adsorbate, a is the adsorption capacity of adsorbent and b is a constant related to the energy adsorption.

Table 4.4: Langmuir Adsorption Isotherm calculations

Dose (g/l)	Initial conc. Co (ppm)	Final conc. Ce (ppm)	Co-Ce (mg/l)	qe (mg/g)	1/Ce	1/qe
10	5	1.13	3.87	0.387	0.884	2.583
10	10	2.72	7.28	0.728	0.367	1.373
10	15	5.0	10	1.0	0.20	1.0
10	20	2.76	17.24	1.724	0.362	0.580

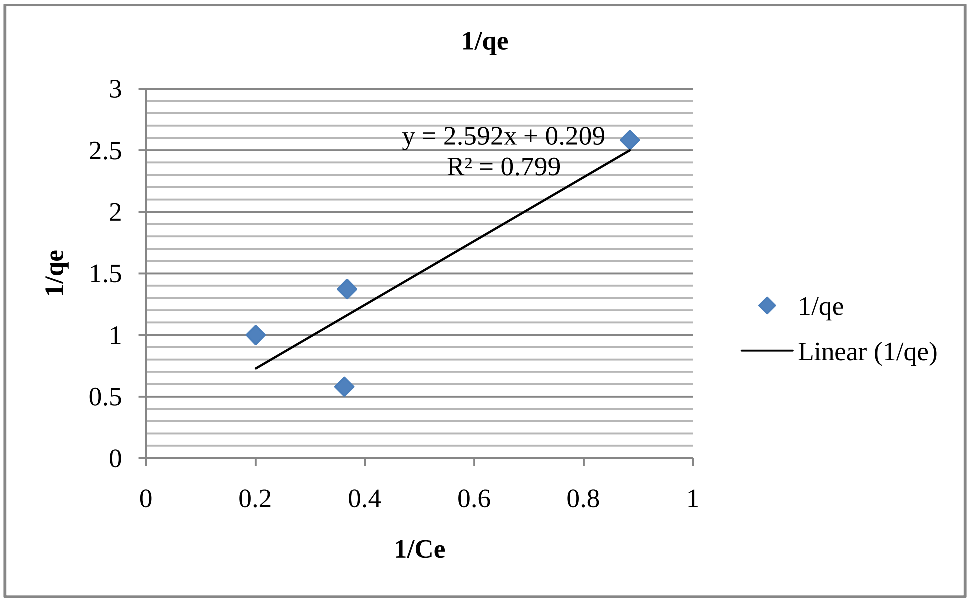


Figure-4.4

Langmuir isotherm model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, time: 45 min)

From figure 4.4 the value of a = 4.780 and b = 0.0807 which is determined from the slope and intercepts of the graph. Coefficient of correlation was 0.7991 which does not indicate Langmuir isotherm fitted well to the experimental data.

4.1.5 Freundlich Adsorption isotherm

The Freundlich model linear form is expressed as:-

$$\text{Ln } q_e = \ln K_f + 1/n \ln c_e$$

Where, Kf =adsorption capacity of adsorbent and n is a constant related to the intensity of adsorption.

Where Ce (mg/l) is the equilibrium concentration of adsorbate

qe (mg/g) is the ratio of fluoride adsorbed to the dosage of the adsorbent, From the graph the value of Kf and n can be calculated. The plot should be straight line.

Value of Kf and n are dependent on different environment factor

Table 4.5: Freundlich Adsorption isotherm

Dose (g/l)	Initial conc. Co (ppm)	Final conc. Ce (ppm)	Co-Ce (mg/l)	qe (mg/g)	Ln Ce	Ln qe
10	5	1.13	3.87	0.387	0.122	-0.949
10	10	2.72	7.28	0.728	1.00	-0.317
10	15	5.0	10	1.0	1.609	0
10	20	2.76	17.24	1.724	1.015	0.544

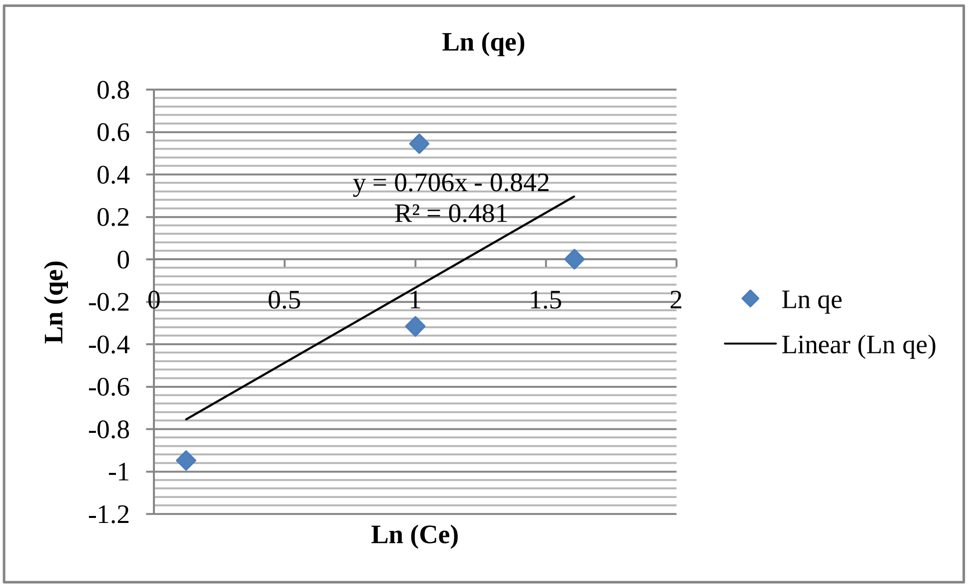


Figure-4.5

Freundlich isotherm model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 45 min)

The coefficient of correlation was 0.4818 and value of n = 1.4152 (adsorption equilibrium constant). The value of KF = – 0.8422 (adsorption capacity measurement mg/g).

4.1.6 Temkin isotherm model

The temkin isotherm model equation is expressed as:-

$$q_e = a + b \log C_e$$

Where qe is the equilibrium adsorption capacity (mg/g), Where Ceis the equilibrium adsorbate concentration (mg/l)

According to this model free energy of adsorbtion is the function of surface area as the area decreases adsorption process reduces. It follows the chemosorbtion of the adsorbate onto the adsorbent.

The experiment was performed at pH 7 and equilibrium time which is 45 min was maintained. Revolutions per minute were 125. The graph is plotted between qe and Log ce.

Table 4.6: Temkin isotherm model

Dose (g/l)	Initial conc. Co (ppm)	Final conc. Ce (ppm)	Co-Ce (mg/l)	LogCe	qe (mg/g)
10	5	1.13	3.87	0.0530	0.387
10	10	2.72	7.28	0.434	0.728
10	15	5.0	10	0.698	1.0
10	20	2.76	17.24	0.440	1.724

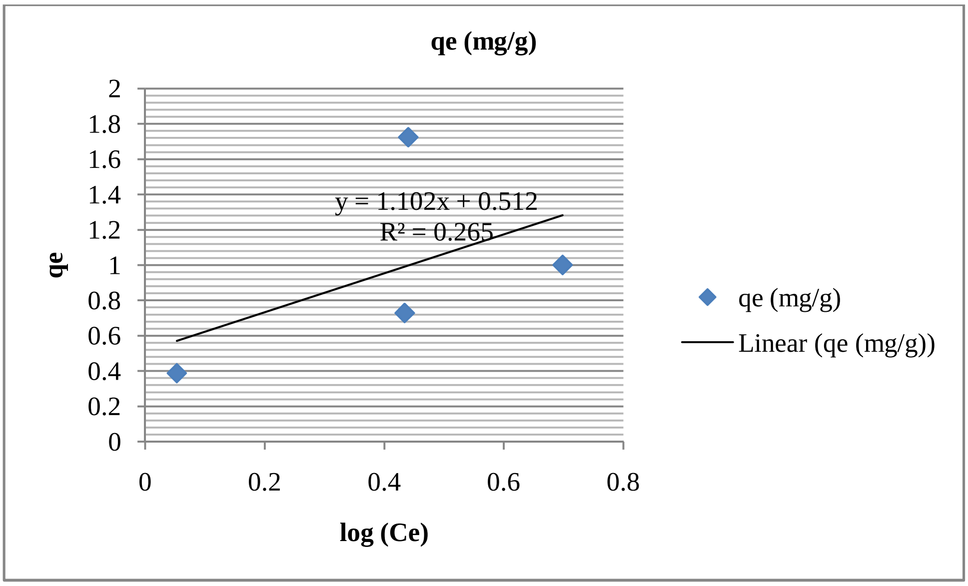


Figure-4.6

Temkin isotherm model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 45 min)

The value of coefficient of correlation was 0.2659 and value of a and b were respectively 0.512 and 1.1021. The values were calculated from slope and intercepts of graph plotted.

Three equilibrium models namely

1. Langmuir
2. Freundlich
3. Temkin

Were applied to find a suitable model equation. These models were linearized and then graph were plotted as shown above. The different constant for these models are calculated and is shown in the tabular foam.

Table- 4.7 : Adsorption isotherms

Isotherms	Parameters	Values
Freundlich	R^2	0.4818
	n	1.4152
	1/n	0.706
	Kf	-0.8422
Langmuir	R^2	0.7991
	a	4.780
	b	0.0807
Temkin	R^2	0.2659
	a	0.512
	b	1.1021

From the above table it can seen that R^2 value for Freundlich, Langmuir, temkin are respectively 0.4818, 0.7991, 0.2659. Therefore Langmuir adsorption isotherm has maximum value of R^2 i.e 0.7991hence this model fitted well among all equilibrium models.

Kinetic model

3.1.7 Pseudo-first order

It was developed by the lagergren to describe the liquid-solid phase adsorption. It is considered one of the earliest model to predict the rate of adsorption on adsorption capacity basis.

The equation is represented as:-

$$\log (q_e-q_t)=\log(q_e)-(K_1/(2.303)t$$

Where qe and qt(mg/g) are the adsorption capacities at equilibrium and time t (min), respectively.

The graph is plotted between log(qe-qt) and time t. The K1 value can be calculated from the graph.

pH was maintained at 7 and rpm 125 and readings were taken at different time interval as shown in the graph

Table 4.8: Pseudo-first order calculations

Time (min)	qe	qt	qe-qt	Log(qe-qt)
10	0.728	0.275	0.453	-0.343
15	0.728	0.39	0.338	-0.471
30	0.728	0.59	0.138	-0.860
45	0.728	0.728	0	-
60	0.728	0.728	0	-
75	0.728	0.728	0	-

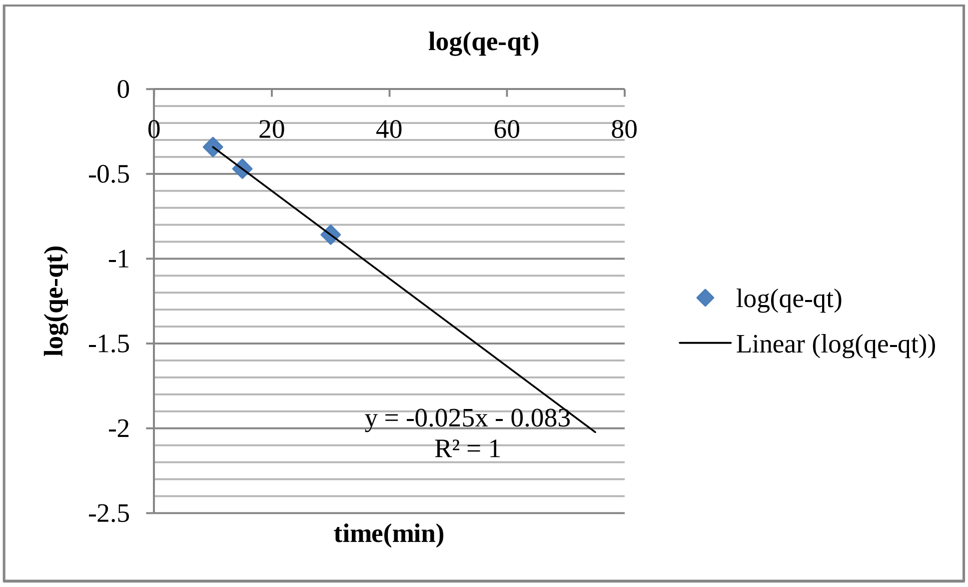


Figure- 4.7

Pseudo first order model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 45 minutes)

4.1.8: Pseudo-second order

The equation of this model is represented by:-

$$t / q_t = 1 / K_2 q_e^2 + t / q_e$$

The graph is plotted between t/qtvs time t. Here K2 is rate constant and it can be calculated from the graph. The plot follows a linear relationship as shown in the graph below. All other values like R^2 is calculated from the graph. All other conditions remaining same just like pH, rpm, and adsorbent dose which was 10g/l.

Table 4.9: Pseudo-second order calculations

Time (min)	qe(mg/g)	qt(mg/g)	t/qt
10	0.728	0.275	36.36
15	0.728	0.39	38.46
30	0.728	0.59	50.84
45	0.728	0.728	61.813
60	0.728	0.728	82.417
75	0.728	0.728	103.021

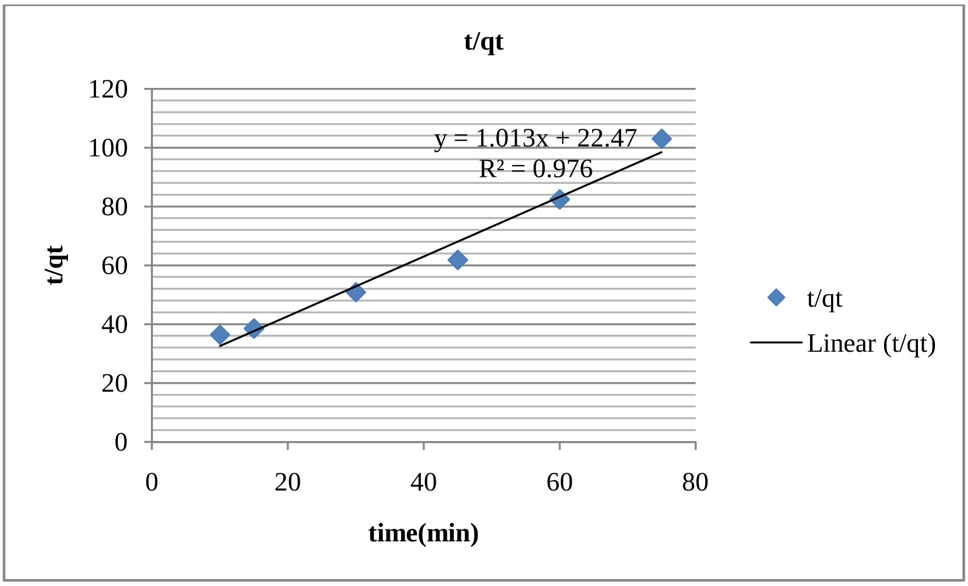


Figure-4.8

Pseudo second order model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 45 minutes)

4.1.9 Intraparticle diffusion model

This model is widely used in the adsorbent-adsorbate system. It was developed by weber and morris(1963). The equation is represented by:-

$$q_t = K_{id}\sqrt{t} + C$$

Were qt is the concentration of sorbed in the time t

Kid is rate constant of intraparticle transport (mg/g/time)

C is the intercept gives idea of the thickness of the boundary layer.

The graph is plotted between qtvs t^0.5. value of r^2 can easily calculated from the graph.

According to this model adsorbate moves to the adsorbent in several steps by pore diffusion, surface diffusion, film or external diffusion or by combination of more than one process.

Table 4.10: Intraparticle diffusion model calculations

Time (min)	qe(mg/g)	t^0.5	qt(mg/g)
10	0.728	3.162	0.275
15	0.728	3.872	0.39
30	0.728	5.477	0.59
45	0.728	6.708	0.728
60	0.728	7.745	0.728
75	0.728	8.660	0.728

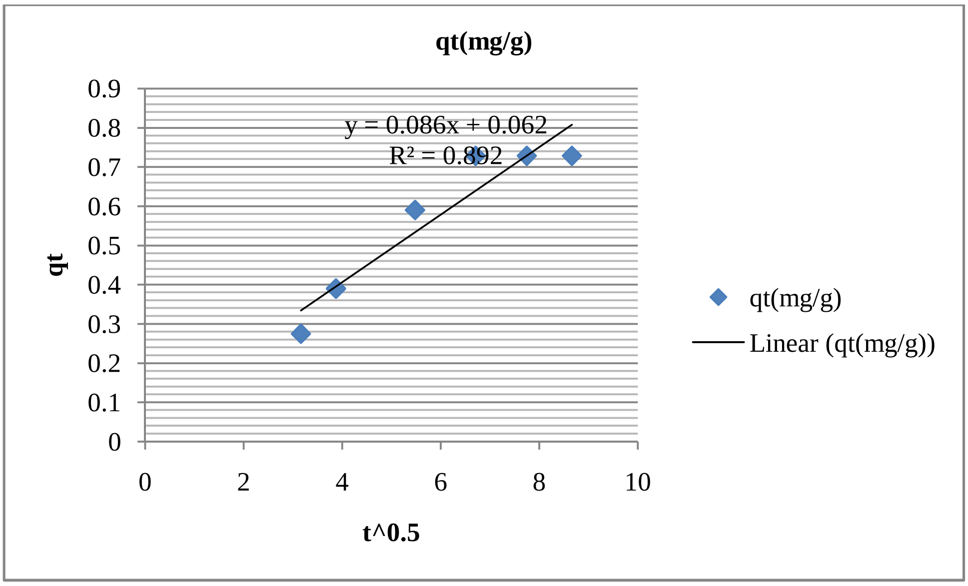


Figure-4.9

Intra particle diffusion model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 45 minutes)

4.1.10 Elovich model

This kinetic model follows chemisorbtion and was developed by zeldowitsch in 1934. This model is also used to describe the adsorption of gas onto the solid system. But now a days it is also used in the aqueous solutions processes of pollution.

It is represented by the equation:-

$$Dq_t/dt = \alpha \exp(-\beta q_t)$$
$$q_{t=} \beta \ln(\alpha \beta) + \beta \ln t$$

The graph is plotted between qtvsln t.

Here α is the initial sorption rate (mg/g/min) wereas β reperesents desorption constant(g/mg).

Table 4.11: Elovich model calculations

Time (min)	qe(mg/g)	lnt	qt(mg/g)
10	0.728	2.302	0.275
15	0.728	2.708	0.39
30	0.728	3.401	0.59
45	0.728	3.806	0.728
60	0.728	4.094	0.728
75	0.728	4.317	0.728

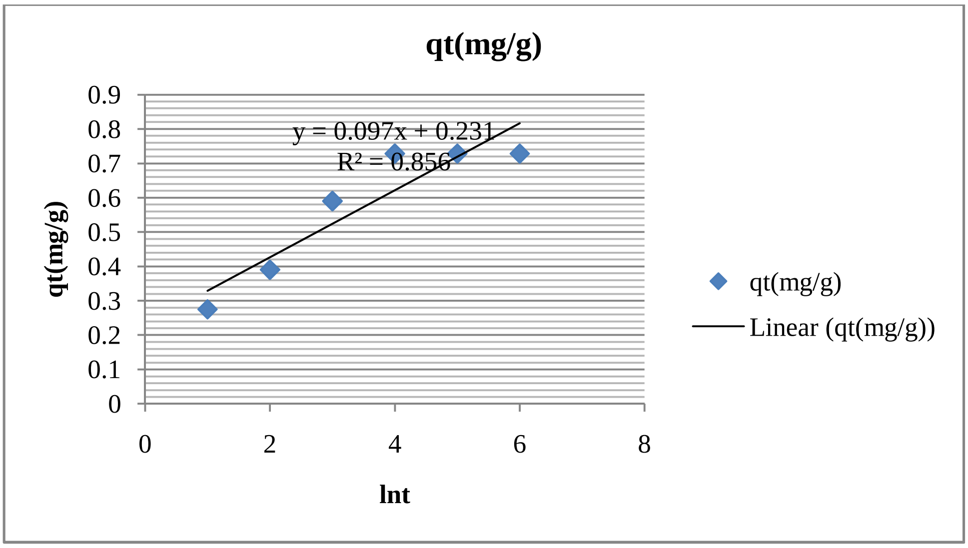


Figure-4.10

Elovich model for adsorption of fluoride on to citrus limetta; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 45 minutes)

Different kinetic models applied below to the adsorption process. All readings and calculations have been shown above in the tabular foam. Kinetic models applied were:-

1. Pseudo-first order model
2. Pseudo-second order model
3. Intra particle diffusion model
4. Elovich model

Various kinetic constants and parameter for the above models have been computed from the values from corresponding graphs of slope and intercept. All values of models are represented in the tabular foam:-

Table-4.12: Kinetic model for citrus limetta (mosambi fruit) pulp powder

Pseudo-first order model			
Co	K1	qe	R^2
10	0.0596	0.824	1
Pseudo-second order model			
Co	K2	qe	R^2
10	0.0456	0.987	0.976
Intra particle diffusion model			
Co	Kid	C	R^2
10	0.0861	0.0621	0.8927
Elovich model			
Co	α	β	R^2
10	109.815	0.0976	0.8569

Co=initial fluoride concentration (mg/l)

From the above table it is clear that value of R^2 is 1, 0.976, 0.8927, 0.8569 for the pseudo-first order, pseudo-second order, intra particle diffusion and Elovich model respectively hence fluoride adsorption is well explained by pseudo-first order model which has maximum R^2 value i.e 1.

4.2 Citrus sinensis (Malta fruit) peel powder

Effect of pH, contact time and initial fluoride concentration were done on citrus sinensis. Different equilibrium and kinetic models was also applied.

4.2.1 Effect of pH on removal of fluoride

Removal of fluoride from drinking water was studied using peel of Malta fruit at different pH range as shown in the table. It was noticed that fluoride removal efficiency increases upto a value of pH 7 and then decreases after that value. It was around 12.8% at pH of around 5 and maximum was observed at the pH 7 which was about 68%, at the pH of 9 removals efficient was 65%. Therefore further experiments were performed at the value of Ph7. In this analysis contact time was 60 min and revolutions per minute were 125. Jar test apparatus was used for all the experiments. Samples were prepared and analyzed for final concentration of fluoride. Variation of fluoride efficiency can be seen from the plotted graph below.

Table 4.13: Effect of pH on removal of fluoride

PH	Co (initial concentration ppm)	Ce (final concentration ppm)	% removal of fluoride
5.34	10	8.72	12.8
7	10	3.21	67.9
9	10	3.55	64.5

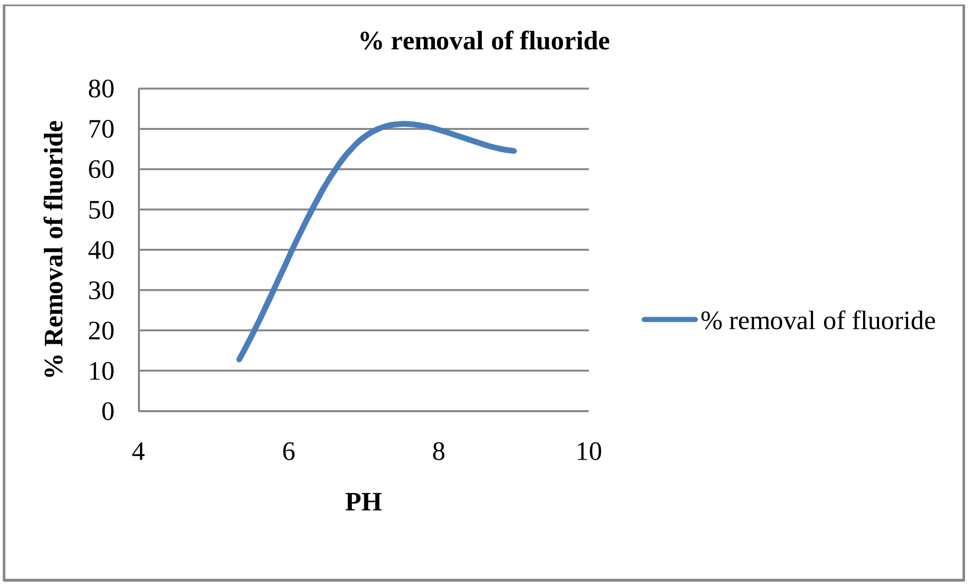


Figure-4.11

Effect of pH on removal of fluoride by citrus sinensis peel powder (process conditions: concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, contact time: 60 minutes)

4.2.2 Effect of contact time

Effect of contact time was studied and it was found that time of concentration was found to be near about 60 minutes. After 60 min efficiency of fluoride removal was almost constant. The study of contact time was done at pH. of 7. It increases from a value of 26.6 % to 69% at about 60 minutes. Beyond this point it was found that there was no effect of contact time on the removal of fluoride. It was notice that at equilibrium curve is parallel to the x-axis.Thevariation in the rate of fluoride removal may be due to reason that initially all surface area of adsorbent wasavailable and concentration of solute was high. After some time, the fluoride adsorption by adsorbent reduced significantly, due to lesser surface area of adsorbent.

Table 4.14: Effect of contact time

Contact time (min)	Co (initial concentration ppm)	Ce (final concentration ppm)	% removal of fluoride
10	10	8.72	12.8
15	10	7.34	26.6
30	10	5.71	42.9
45	10	4.23	57.7
60	10	3.21	67.9
75	10	3.19	68.1

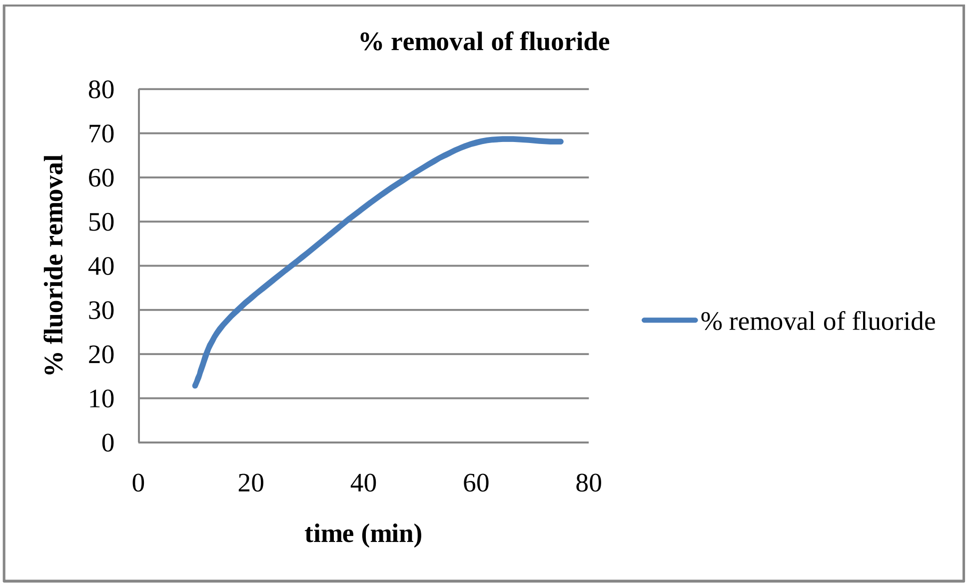


Figure-4.12

Effect of time on removal of fluoride by citrus sinensis peel powder (process conditions: concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, pH: 7)

4.2.3 Effect of initial fluoride concentration

Experiment was done to know the specific uptake of fluoride by the adsorbent. Concentration of the fluoride was varied from 5mg/l to 20mg/l and it can be seen in the graph that adsorption of ions increases as the fluoride concentration increases. The graph almost followed a linear relationship which shows that adsorption is directly proportional with the value of initial concentration of fluoride. The fluoride value in the ground water is generally below 5mg/l and at this value final adsorbtion value was 0.126mg/l which is well below 1.5mg/l hence peel of malta can be used for removal of fluoride effectively from water.

Table 4.15: Effect of initial fluoride concentration

Initial fluoride concentration (ppm)	Final fluoride concentration (ppm)	qe
5	3.74	0.126
10	3.21	0.679
15	5.18	0.982
20	6.01	1.399

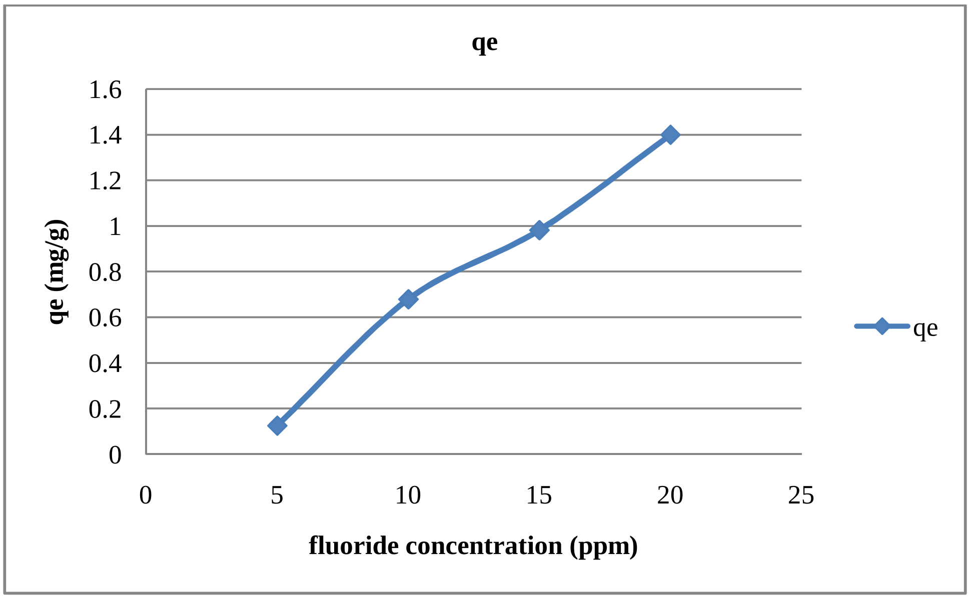


Figure-4.13

Specific uptake of fluoride by citrus sinensis peel powder (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 60 min)

4.2.4 Langmuir Adsorption Isotherm

The linear form is expressed as follows

$$1/q_e = 1/a + 1/ab\ c_e$$

Where qe (mg/g) is the ratio of fluoride adsorbed to the dosage of the adsorbent, Ce (mg/l) is the equilibrium concentration of adsorbate, a is the adsorption capacity of adsorbent and b is a constant related to the energy adsorption

According to the equation the adsorption of monolayer takes place on homogeneous sorption sites of equal energy

Table 4.16: Langmuir adsorption isotherm calculations

Dose (g/l)	Initial conc. Co (ppm)	Final conc. Ce (ppm)	Co-Ce (mg/l)	qe (mg/g)	1/Ce	1/qe
10	5	3.74	1.26	0.126	0.267	7.936
10	10	3.21	6.79	0.679	0.311	1.472
10	15	5.18	9.82	0.982	0.193	1.018
10	20	6.01	13.99	1.399	0.166	0.714

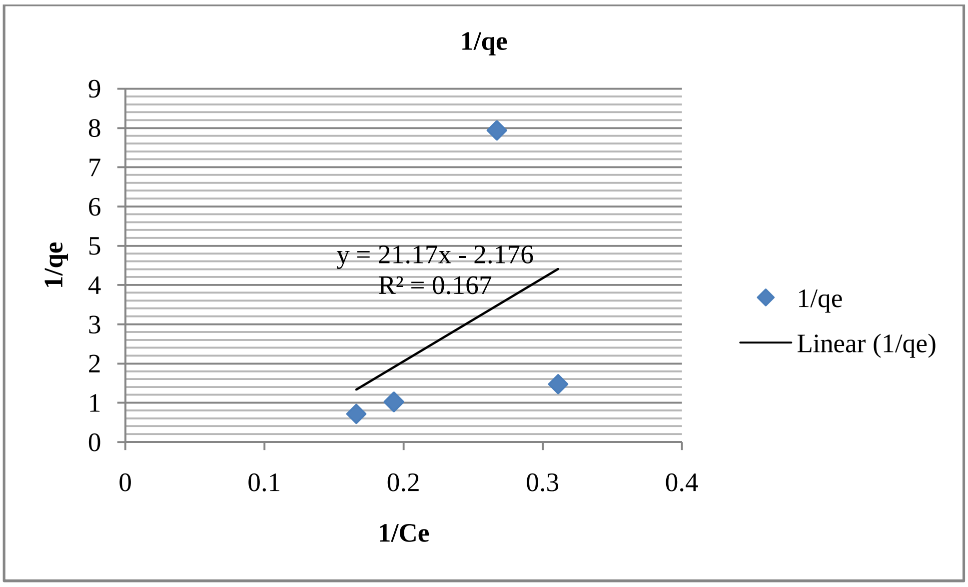


Figure-4.14

Langmuir isotherm model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, time: 60 min)

4.2.5 Freundlich Adsorption isotherm

The linear form is represented by the following equation

$$\text{Ln } q_e = \ln K_f + 1/n \ln c_e$$

Where, Kf is the adsorption capacity of adsorbent and n is a constant related to the intensity of adsorption.

Where qe (mg/g) is the ratio of fluoride adsorbed to the dosage of the adsorbent, Ce (mg/l) is the equilibrium concentration of adsorbate

From the graph the value of Kf and n can be calculated. The plot should be straight line.

Value of Kf and n are dependent on different environment factors.

Table 4.17: Freundlich adsorption isotherm calculations

Dose (g/l)	Initial conc. Co (ppm)	Final conc. Ce (ppm)	Co-Ce (mg/l)	qe (mg/g)	**Ln Ce**	**Ln qe**
10	5	3.74	1.26	0.126	1.319	-2.071
10	10	3.21	6.79	0.679	1.166	-0.387
10	15	5.18	9.82	0.982	1.644	-0.018
10	20	6.01	13.99	1.399	1.793	0.335

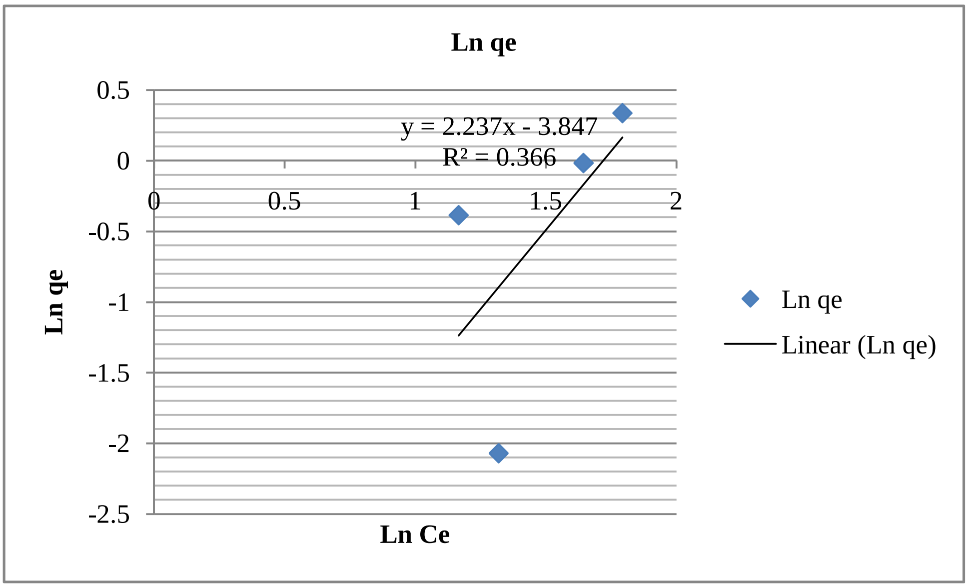


Figure-4.15

Freundlich isotherm model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 60 min)

4.2.6 Temkin isotherm model

The equation model is represented by the following equation:-

$$q_e = a + b \log C_e$$

Where qe is the equilibrium adsorption capacity (mg/g)

Where Ce is the is the equilibrium adsorbate concentration (mg/l)

According to this model free energy of adsorbtion is the function of surface area as the area decreases adsorption process reduces. It follows the chemosorbtion of the adsorbate onto the adsorbent.

The experiment was performed at pH 7 and equilibrium time which is 45 min was maintained. Revolutions per minute were 125.

The graph is plotted between qe and Log ce.

Table 4.18: Temkin isotherm calculations

Dose (g/l)	Initial conc. Co (ppm)	Final conc. Ce (ppm)	Co-Ce (mg/l)	LogCe	qe (mg/g)
10	5	3.74	1.26	0.572	0.126
10	10	3.21	6.79	0.506	0.679
10	15	5.18	9.82	0.714	0.982
10	20	6.01	13.99	0.778	1.399

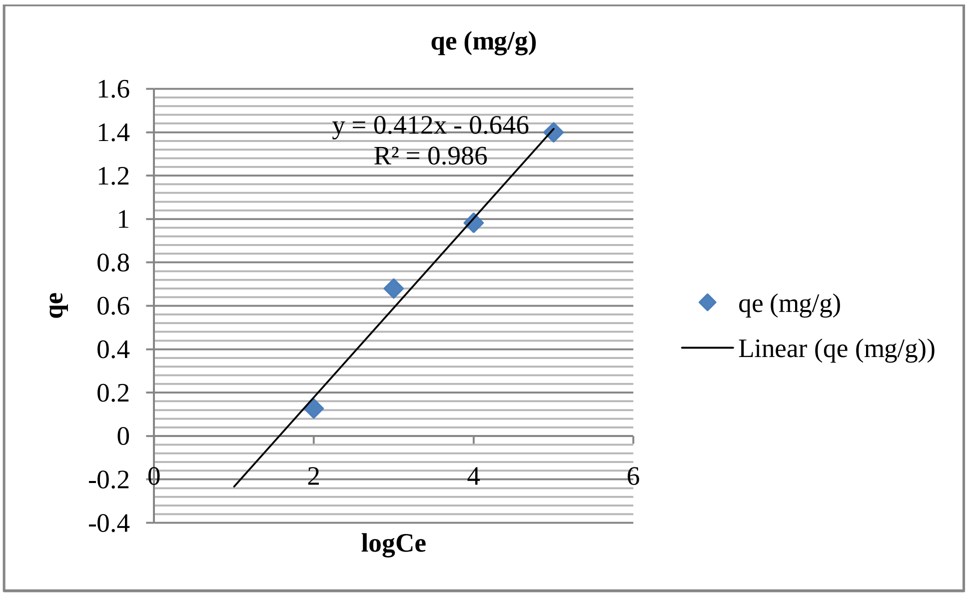


Figure-4.16

Temkin isotherm model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, rpm: 125, Time: 60 min)

Three equilibrium models namely

1. Langmuir
2. Freundlich
3. Temkin

Were applied to find a suitable model equation. These models were linearized and then graph were plotted as shown above. The different constant for these models are calculated and is shown in the tabular foam.

Table-4.19: Adsorption isotherms

Isotherms	Parameters	Values
Freundlich	R^2	0.3665
	n	0.4469
	1/n	2.2372
	Kf	0.0213
Langmuir	R^2	0.1675
	a	-0.459
	b	-0.102
Temkin	R^2	0.9869
	a	-0.646
	b	0.412

From the above table it can be seen that R^2 value for Freundlich, Langmuir, temkin are respectively 0.3665, 0.1675, 0.9869. Therefore temkin adsorption isotherm has maximum value of R^2 i.e 0.9869 hence this model fitted well among all equilibrium models

Kinetic models

4.2.7 Pseudo-first order model

lagergren developed this to describe the liquid-solid phase adsorption. It is considered one of the earliest models to predict the adsorption rate depending on the adsorption capacity.

The equation is represented as:-

$$\log(q_e - q_t) = \log(q_e) - (K_1/(2.303)t$$

The graph is plotted between log(qe-qt) and time t. The value K1 can be calculated from the graph.

pH was maintained at 7 and rpm 125 and readings were taken at different time interval as shown in the graph

Table 4.20: Pseudo-first order model calculations

Time (min)	qe (mg/g)	qt (mg/g)	qe-qt (mg/g)	Log(qe-qt)
10	0.679	0.128	0.551	-0.258
15	0.679	0.266	0.413	-0.384
30	0.679	0.429	0.25	-0.602
45	0.679	0.577	0.102	-0.991
60	0.679	0.679	0	-
75	0.679	0.679	0	-

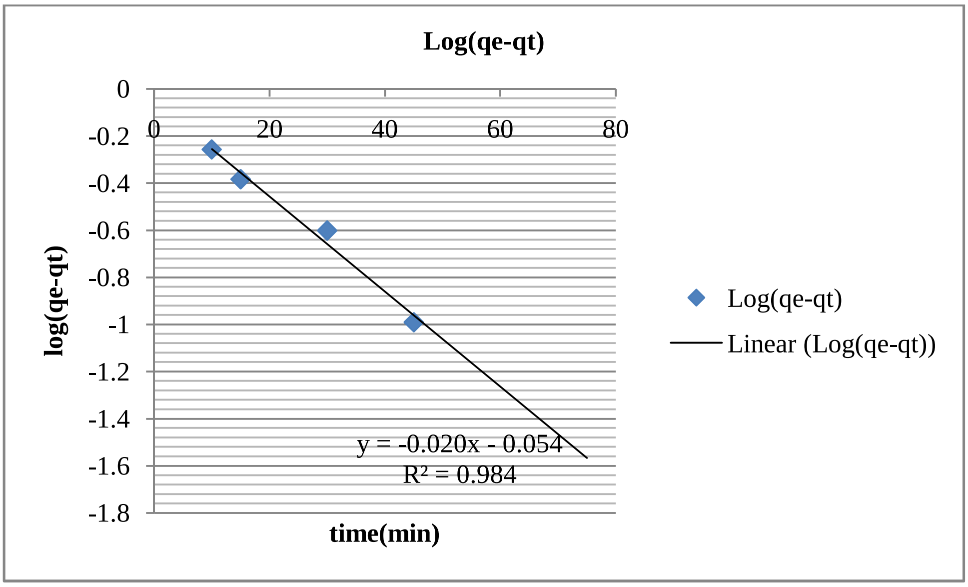


Figure-4.17

Pseudo first order model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 60 minutes)

4.2.7 Pseudo-second order

The equation is represented by:-

$$t / q_t = 1 / K_2 q_e^2 + t / q_e$$

The graph is plotted between t/qtvs time t

Here K2 is rate constant and it can be calculated from the graph. The plot follows a linear relationship as shown in the graph below. All other values like R^2 is calculated from the graph. All other conditions remaining same just like pH, rpm, and adsorbent dose which was 10g/l.

Table 4.21: Pseudo-second order calculations

Time (min)	qe(mg/g)	qt(mg/g)	t/qt
10	0.679	0.128	78.125
15	0.679	0.266	56.390
30	0.679	0.429	69.930
45	0.679	0.577	77.989
60	0.679	0.679	88.360
75	0.679	0.679	110.45

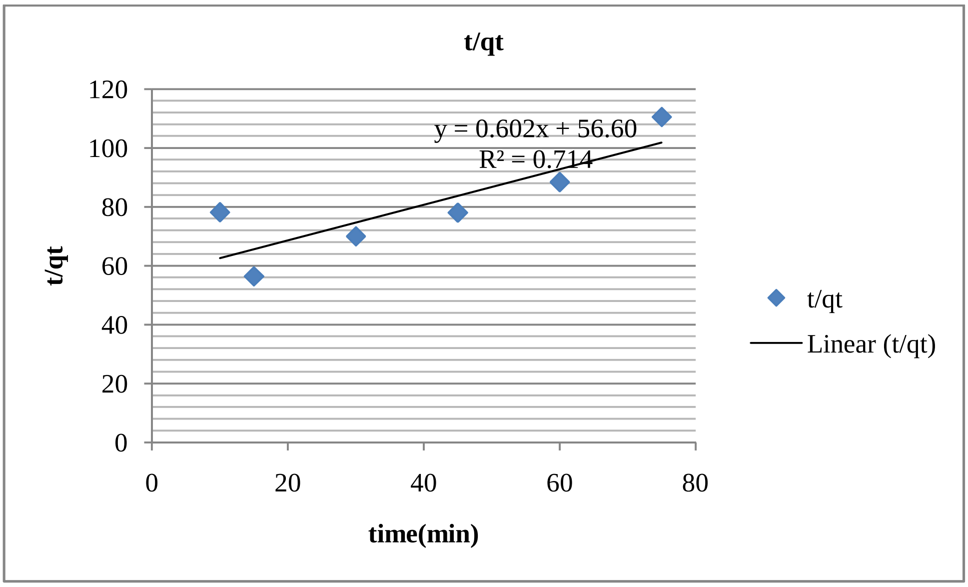


Figure-4.18

Pseudo second order model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 60 minutes)

4.2.8 Intraparticle diffusion model

This model is widely used in the adsorbent-adsorbate system. It was developed by weber and morris(1963). The equation is represented by:-

$$q_t = K_{id}\sqrt{t} + C$$

Were qt is the concentration of sorbed in the time t

Kid represent rate constant of the intraparticle transport (mg/g/time)

C is the intercept gives idea about the thickness of the boundary layer.

The graph is plotted between qtvs t^0.5. value of r^2 can easily calculated from the graph.

According to this model adsorbate moves to the adsorbent in several steps by pore diffusion, surface diffusion, film or external diffusion or by combination of more than one process.

Table 4.22: Intraparticle diffusion model calculations

Time (min)	qe(mg/g)	t^0.5	qt(mg/g)
10	0.679	3.162	0.128
15	0.679	3.872	0.266
30	0.679	5.477	0.429
45	0.679	6.708	0.577
60	0.679	7.745	0.679
75	0.679	8.660	0.679

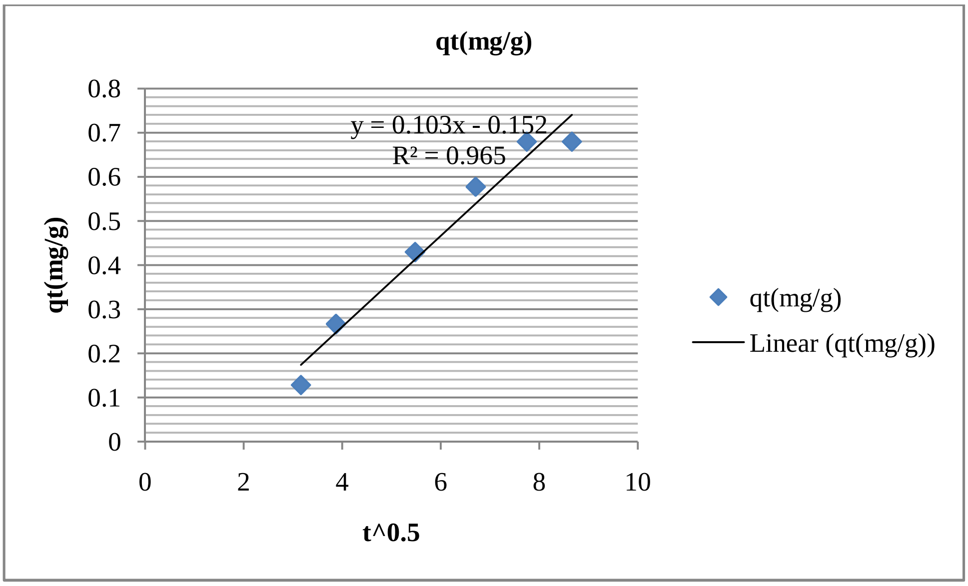


Figure-4.19

Intra particle diffusion model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 60 minutes)

4.2.9 Elovich model

This kinetic model follows chemisorbtion and was developed by zeldowitsch in 1934. This model is also used to describe the adsorption of gas onto the solid system. But now a days it is also used in the aqueous solutions processes of pollution.

It is represented by the equation:-

$$Dq_t/dt = \alpha \exp(-\beta q_t)$$

$$q_{t=} \beta \ln(\alpha \beta) + \beta \ln t$$

The graph is plotted between qtvsln t.

Here β represents desorption constant(g/mg) and α is the initial sorption rate(mg/g/min).

Table 4.23: Elovich model calculations

Time (min)	qe (mg/g)	lnt	qt(mg/g)
10	0.679	2.302	0.128
15	0.679	2.708	0.266
30	0.679	3.401	0.429
45	0.679	3.806	0.577
60	0.679	4.094	0.679
75	0.679	4.317	0.679

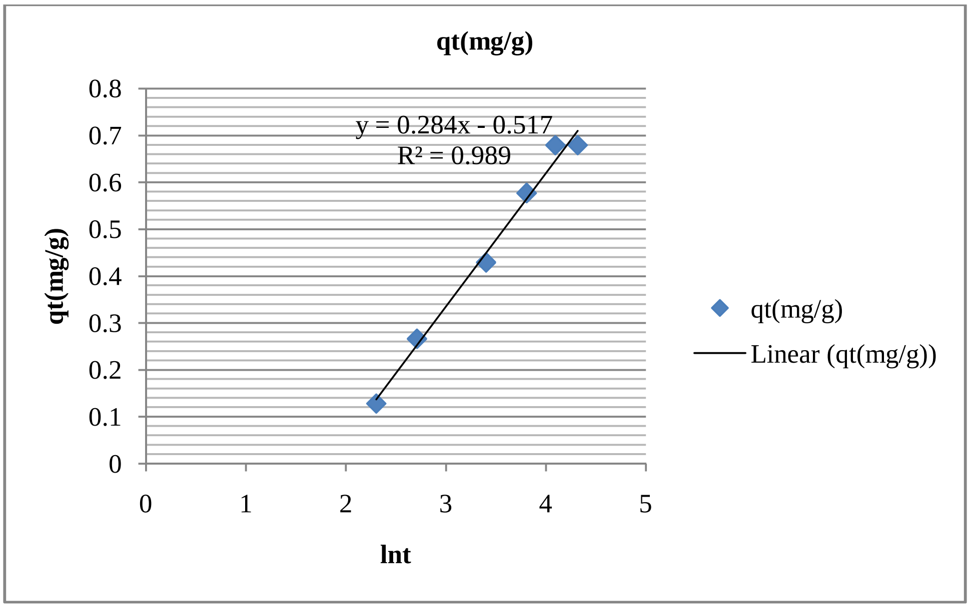


Figure-4.20

Elovich model for adsorption of fluoride on to citrus sinensis; (process conditions: pH: 7, concentration of adsorbents: 10g/L, initial concentration of fluoride: 10mg/L, rpm: 125, Time: 60 minutes)

Adsorption process was explained by kinetic models. Readings and calculations have been shown above in the tabular foam. Kinetic models applied were:-

1. Pseudo-first order model
2. Pseudo-second order model
3. Intra particle diffusion model
4. Elovich model

Various kinetic constants and parameter for the above models have been computed from the slope as well as intercept of the corresponding graphs. All values of models are shown in the tabular foam:-

Table-4.24: Kinetic model for citrus sinensis (malta fruit) peel powder

Pseudo-first order model			
Co	K1	qe	R^2
10	-0.0467	0.881	0.9842
Pseudo-second order model			
Co	K2	qe	R^2
10	0.00641	1.659	0.7142
Intra particle diffusion model			
Co	Kid	C	R^2
10	0.103	-0.152	0.9651
Elovich model			
Co	α	β	R^2
10	0.5695	0.2843	0.9890

Co=initial fluoride concentration (mg/l)

From the above table it is clear that value of R^2 is 0.9842, 0.7142, 0.9651, 0.9890 for the pseudo-first order, pseudo-second order, intra particle diffusion and Elovich model respectively hence fluoride adsorption is well explained by Elovich model which has maximum R^2 value i.e 0.9890.

Chapter 5

CONCLUSION

In the present study two adsorbent i.e mosambi fruit pulp powder and Malta fruit peel powder is taken to study the removal of fluoride from drinking water. Batch experiments were carried out to study the effect of agitation time and initial fluoride concentration. Before this a value of pH at which maximum removal efficiency was found and other experiments were at that pH only. The summary of both the materials is given below:-

5.1 Citrus limetta (Mosambi fruit) pulp powder: -

First of all a pH value of 7 was found. At this value of pH we got maximum efficiency for removal of fluoride. After this effect of contact time and initial fluoride concentration experiments were carried out. In this case we got a equilibrium time of around 45 minutes after it there was no effect of time on removal of fluoride and graph becomes parallel to x-axis.Whereas in case of initial fluoride concentration experiment we obtain almost a linear relationship when the graph was plotted between concentrations of fluoride vs. qe (mg/g).

R^2 is 1, 0.976, 0.8927, 0.8569 for the pseudo-first order, pseudo-second order, intra particle diffusion and Elovich model respectively. The adsorption kinetics is well presented by the pseudo-first order rate equation which has maximum R^2 value i.e. 1.

R^2 value for Freundlich, Langmuir, temkin are respectively0.4818, 0.7991, 0.2659. Langmuir adsorption isotherm has maximum value of R^2 i.e. 0.7991hence this model fitted well among all equilibrium models.

The value of the fluoride in the ground water is generally below 5mg/l and at this value final adsorption value was 1.13mg/l which well below 1.5mg/l hence this adsorbent can be used for the removal of fluoride from drinking water.

5.2 Citrus sinensis (Malta fruit) peel powder: -

In this case also we got a pH value of 7 at which maximum removal was possible. Similar experiments were carried out as in case of mosambi pulp. Here a equilibrium time of around 60 minutes after it there was no effect of time on removal of fluoride and graph becomes parallel to x-axis.R^2 value for Freundlich, Langmuir, temkin are respectively 0.3665, 0.1675, 0.9869. Therefore temkin adsorption isotherm has maximum value of R^2 i.e. 0.9869 hence this model fitted well among all equilibrium models.

Whereas in case of kinetic models value of R^2 is 0.9842, 0.7142, 0.9651, 0.9890 for the pseudo-first order, pseudo-second order, intra particle diffusion and Elovich model respectively hence fluoride adsorption is well explained by Elovich model which has maximum R^2 value i.e. 0.9890.

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