Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent

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Abstract

Fluoride is an essential constituents for both humans and animals depending on the total amount ingested or its concentration in drinking water. The presence of fluoride in drinking water, within permissible limits of 0.5-1.0 mg/l, is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental and skeletal fluorosis. An attempt is made to study the various materials available with special reference to different methods of defluoridation and different natural adsorbents used for defluoridation by adsorption technique. Different activated adsorbent samples like activated alumina, activated bauxite, Activated rice husk were taken and equilibrium studies were conducted to find a suitable adsorbent. The results obtained from these studies are presented in this report.

Key words: Alumina, adsorption defluorination.

Introduction

Fluoridre is a normal constituent of natural water samples. Consumption of water having excess fluride over a prolonged period leads to a chronic ailment known as fluorosis. Fluorosis isa crippling disease affecting bones, teeth and soft tissues. Fluoride enters the body through food, water, drugs, industrial exposure etc. Drinking water is the major contributor (75-90% of daily intake). The major sorces of fluoride in ground water are fluoride bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxylapatite. The fluoride contene in the ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature ,concentration of calcium and bicarbonate ions in water. The fluoride levels in industrial emission and waste water were exhibited in table 1

Table-1
Estimated Total Inorganic Fluoride Emission from Major industries

Sources	Emission Tons/year
Steel	40,100
Ceramics	21,200
Phosphate fertilizer and processing industries	18.700
Aluminum industries	16,000
Combustion of coal	16,000
Non-ferrous metal foundries	4,000

Table-2
Summarized Information on the Occurrence of Excessive Fluoride in Ground Water In India

State	No. of Habitation with excess fluoride	State	No. of Habitation with excess fluoride
Andhra Pradesh	7548	Madhya Pradesh	201
Gujarat	2378	Orissa	1138
Karnataka	860	Punjab	700
Kerla	287	Rajasthan	16560
Meghalaya	33	Tamilnadu	527
Haryana	334	Uttar Pradesh	1072
Himachal Pradesh	488	West Bengal	21

Table -3
Permissible Limit of Fluoride in Drinking Water Prescribed by Various Organizations

Name of the organization	Permissible limit of fluoride ion (ppm)
(International standard for drinking water)	0.5
U.S. Public Health Standard	0.8
The committee on public health engineering manual and code of practice Govt. of India	1.0
Indian council of medical research recommendation	1.0
ISI recommendation	1.5

Skeletal Effects: Crippling skeletal fluorosis, which is associated with the higher level of exposure, can result from osteosclerosis, ligamentous and endinous calcification and extreme bone deformity. Evidence from occupational exposure also indicate that exposure to elevated concentration of fluoride in the air may also be a cause of skeletal fluorosis

Effect of fluoride on teeth and bones: The beneficial and the detrimental effects of fluoride naturally present in water were well established by the early 1940s. High levels of fluoride present in concentrations up to 10 mg/l were associated with dental fluorosis (yellowish or brownish striations or mottling of the enamel) while low levels of fluoride, less than 0.1 mg/l were associated with high levels of dental decay, although poor nutritional status is also an important contributory factor. The level of dental caries from seven at a fluoride concentration of 0.1 mg l^{-1} to around 3.5 at a fluoride concentration of 1.0 mg l^{-1}. As fluoride concentration increased further(upto 2.6 mg l^{-1}) dental decay continues to fall, but only slightly.

Zipkin and McCurle have reported that ingested NaF, Na_3SiF_6, and Na_2PO_3F produced deposits of fluoride in bones and teeth. Analysis of selected bones and skeletal tissues obtained from individuals who are ingesting waters containing 0.4 to 1 ppm for at least 10 years contained up to 0.548% F on an ash basis. Accumulation of fluorides in human body results in pain in bones and joints and outward bending of legs from the knees which is known as knock knee syndrome.

Behavior of fluoride with other ions: The correlation studies provide an insight about the behavior of different ions with F and which of these ions controls the F concentration in ground water. F shows negative correlation with most of the ions (Ca, Mg, Na, K, Cl). The ions having negative correlation with F are those which affect the fluoride in water and vice versa are the ones with positive correlation. The groundwater where the F concentration is high, bicarbonates and carbonates are predominant anions and the water is alkaline. Therefore, high F waters are having more alkalinity, over hardness and are low calcium waters.

Material and Methods

Several methods have been suggested from time to time for removing excess fluorides from water. The various materials studied for defluoridation include, clays, ion-exchange resins, activated carbons, sulfonated coals, magnesium compounds, turpentine, iron and aluminum salts. Bulusu[1] studied various techniques for the defluoridation of water, in this section these defluoridations techniques are reviewed.

Activated Carbon Treatment: Bhakuni and Shastry[2] studied the defluoridation of water using carbon from saw dust. They found that defluoridation capacity was 350-450 mg per kg of dry carbon, when the optimum fluoride of 270

liters/min, was maintained. But ions other than fluorides particularly chlorides and sulfate ions reduced the capacity of carbon. Balinski and Wlodzimerz[3] studied defluoridation using different kinds of activated carbon under static and dynamic conditions. Highest adsorption properties were observed in carbons with lower pH of Water.

Alum Treatment (Nalgonda Technique): It was investigated by many researchers that, the chemical precipitation of fluoride by use of multivalent metal ions. Boruff, Gulp and Stotlenbery, T.S. Bhakuni and N.N.Sharma reported that activated carbonized sawdust can be used in the defluoridation of water. The promising results were obtained when the carbonized material was either quenched or soaked in 2% $Al_2(SO_4)_3$) solution and with less satisfactory results when 2% of K-alum was used. The amount of fluoride adsorbed was proportional to the initial concentration of the solution and optimum quantity or adsorbent can be reached for a given concentration. Other ions normally present in water did not appear to effect defluoridation. Adsorption was increased by a decrease in temperature. The carbon can be reactivated by treating with- 0.2% to 0.5 $Al_2(SO_4)_3$, for 15 min. The results among various researchers on alum coagulant varied considerably. Though the Nalgonda Technique have shown that the aluminum sulfate treatment effectively remove fluoride. The satisfactory performance of the $2270m^3$ per day plant at Kaderi in treating 4.22-4.8 mgF/ltr,at a cost of Rs.1.15/m^3.

Distillation Filtration: There are commercially available distillation filters that can be purchased to remove fluoride from water. On a related note when looking at bottled water, keep in mind that 'distilled water' does not imply that a product is suitable for drinking water and other undesirable impurities may be present.

Defluoridation Of Water Using Activated Alumina As An Adsorbent: Activated Alumina is the most accepted and proved for fluoride removal from dinking water Rubel and Wooley[4] worked out the cost of defluoridation as 2-5 cents per m^3.The use of activated alumina regenerated by acid ,alkali and even better by alum.

E.F.Zolovite carried out defluoridation of drinking water over activated alumiana in a pilot scale. At the start of the filtration F is almost completely eliminated. When the concentration of fluoride raises 1-15 mg/lit. The filter is regenerated with $Al_2(SO_4)_3$ solution. By mixing the filtrate with raw water, a concentration of 0.821mgF/ltr may be maintained. A pilot plant yielded 1200-1500m^3 water per fourteen hours.

As defined by Rao activated alumina is a granular, highly porous material consisting essentially of aluminium trihydrate. It effectively removes fluoride from drinking water, based on the principle of adsorption. The removal

capacity of the medium ranges between 1400 – 1800 mg/kg, depending on the grade used (ND, 2006). The ability to remove fluoride also depends on the raw water quality and characteristics such as hardness can alter the effectiveness of the treatment process. After removing a certain amount of fluoride from the drinking water, the material becomes saturated with adsorbed fluoride and the capacity to remove fluoride further is reduced. The adsorbed fluoride must then be washed off chemically (using hypochlorite acid, sulphuric acid, alum or sodium hydroxide), in a process known as regeneration. The used activated alumina can be reused after regeneration up to 10 – 12 times (ND, 2006). It should be noted that using sodium hydroxide to regenerate the activated alumina requires neutralization to remove any residual sodium hydroxide from the bed, as the treatment process is pH dependent. As the alkalinity of the raw water increases, the efficiency of the activated alumina decreases. The main disadvantages of activated alumina as a defluoridation technique are the cost of regeneration and operational and maintenance issues (Ganeshi et al, 2003). The fluoride-rich effluent from the cleaning process must also be disposed of carefully to avoid contamination (UNICEF, updated.

In their study of Chari K.V., Rao R.J.[5] they found that activated alumina As an excellent adsorbent for removal of fluoride from water of various composition and lowering the fluoride level to <1 mg/lit, which is in accordance with maximum admissible concentration level for drinking water, is readily achieved by activated alumina. The removal of fluoride from Industrial waste more than 96%.The possible removal of fluoride by impregnated alumina can be explained by ion exchange method and hydroxide group on the surface material. It is observed that to reduce the fluoride concentration to low level, activated alumina is the most popular and effective because of ease of application and low cost.

In their study of Ast. D Smith D[6] found that activated alumina shows the removal efficiency up to 96% at the optimized condition of various parameters viz, pH, temp, concentration, and dose of activated alumina.

The same result was obtained when Alagarasm S.R[7] and co workers used activated alumina for batch study as a defluoridation medium. The study concluded that the rate of adsorption was observed maximum initially and slowly approaches to equilibrium. They also observed that the adsorption of fluoride from water should be relatively more rapidly than the more dilute solution, the adsorption isotherm follows Freundlich and Langmuir adsorption isotherm.

Shortt H. Mc Robert[8] and co workers, used the ion exchange resin and activated alumina as a defluoridation media and found the equilibrium adsorption capacity of ion exchange resin of indion-100 was 1.54gm/Kg of resin. Two hundred bed volumes of water can be treated with initial fluoride ion

concentration of 202 ppm to obtained an effluent concentration of less than 1.0ppm at the optimized fluid flow rate of 35 liter/hr. Both TDS and alkinity of the treated water decreased during the defluoridation treatment but no appreciable change was observed in the taste of water Bulsu K.R. and W.G.Nawalakhe[12] studied the adsorption kinetics of adsorption of defluoridation with pulverized activated alumina, ACC,G-80. They reported that i) initial rate of adsorption of fluoride decreased progressively after the initial 30min. and give rather the slow approach to equilibrium. ii) The adsorption isotherm poorly confirms the Freundlich and Langmuir isotherm. iii) By employing BET equation and analyzing very good linearization is observed. iv) The rate of defluoridation decreased with increase in the pH of the water.

Determination of Fluoride: More than 50 methods of determination of fluoride in water have been reported in Literature. Significant methods are briefly discussed.

(a) Spectrophotometric Methods: David Ravinson and John M. Harley[9] has reported a modified spectrophotometric analysis based on the fact that F^- prevents the full color development of a Th-Chrome Azurols lake. This method permits the determination as little as 0.1 ppm. of fluoride. A rapid determination of fluoide is presented by Stephen Magregain which employs the reaction between Zr^{4+} and Erichrome cyanine R for color formation and subsequent bleaching of lake by F^-. The method based on the bleaching of thorium alizarin, lake by F is presented by Icken and Blank[10]. Modified thorium alizarin reagents permit measurements by means of a spectrophotometer or a photoelectric colorimeter. The method eliminates the errors Inherent in the usual visual it ration and provides for accurate estimation of F^- in the range of 0-1.25 ppm of sample.

Electrolysis Method: Have reported a method for the determination of microgram quantities of fluoride and cyanide by measurement of current from spontaneous electrolysis. A coiled 99.99% pure Al anode and Ft cathode in 0.2 M NaOH are used to determine F. The current is read 2 min after addition of F solution. For less than 5 ppm F 0.017 M Benzoic acid is used as an electrolyte.

Colorimetric Method: The following method is reported by Thomas and Chamberlain[11]:

A sample of the compound which has been previously dried over P_2O_5 and which is sufficient to give 10-40 ppm of F on combustion is deposited on ash less filter paper which is folded in such a manner that it can be suspended from a Ft spiral. The paper is dipped in a 250ml flask containing approximately 30ml distilled water. After combustion, the solution is allowed to stand for 10 min. with occasional shaking. The solutions and washings are then transferred to 100ml volumetric flask along with 10ml. 0.0005M alizarin complex solution, (1.2-dihydroxy anthraquinone 3 phenyl methylmamine-N. N diacetic acid) and 2 ml. of pH 4.3 acetate

buffer. After dilution to approximately 75ml., 10 ml. 0.005 m Ce(III) is added with swirling, then the solution is diluted to 100 ml and allowed to stand for 1 hr. protected from light and drafts. The optical density of the solution is determined in 4 cm. cell at 610 nm against blank containing only reagents, within the range 15-50 ppm the absolute accuracy is +0.51. When the compound contains CF_3, groups, the sample should be covered with 1 mg. of $KC1O_3$ before it is folded into the paper. There is no interference from other halides, Sulfates or nitrates.

Gravimetric method: An easily filtered CaF_2. ppt. is obtained by adding 2ml 0.2N NaOH and 5ml. 20% $CaCl_2$ solution to 25 ml of the test solution, heating almost to boiling (to a rapid evolution of very Pine bubbles) rapidly cooling with running water, and then filtering after the addition of filter paper pulp.

Scope and objective of present study: Since fluorosis is incurable, prevention is the only way to control this public health hazard. A partial solution is to provide an alternative and safe drinking water to endemic areas by the following ways.

a) Water to be imported preferably from a surface source by long pipeline supply, and is feasible not all times.

b) In the places where such supply is not feasible defluoridation of available high fluoride water becomes necessary.

Activation of natural adsorbents: (a) Activation of Bauxite: Bauxite activation process involves a thermal pre-treatment designed to make the valuable alumina phases (gibbsite and boehmite) amorphous. The benefit of this process is that subsequent Bayer processing can be done under less severe conditions (especially temperature), allows more effective extraction of the boehmitic phases, reduced operating temperatures and costs. The heat treatment is relatively low temperature (~500–550°C) for a short time (i.e. flash calcining) and thus the kaolin is unaffected (a portion of the kaolin might start dehydration to meta-kaolinite, but this does not significantly affect its reactivity and desilication characteristics). Activation of bauxite results in changes to both the physical and chemical properties of the ore. The changes arise from decomposition of hydrated mineral phases in bauxite and also volatilisation of organic carbon, with the result being a form of bauxite that exhibits distinctly different reactivity to the original. The potential advantages afforded by activated bauxite toward both mitigating carbon-related processing problems and facilitating more cost-effective processing of boehmitic ore.
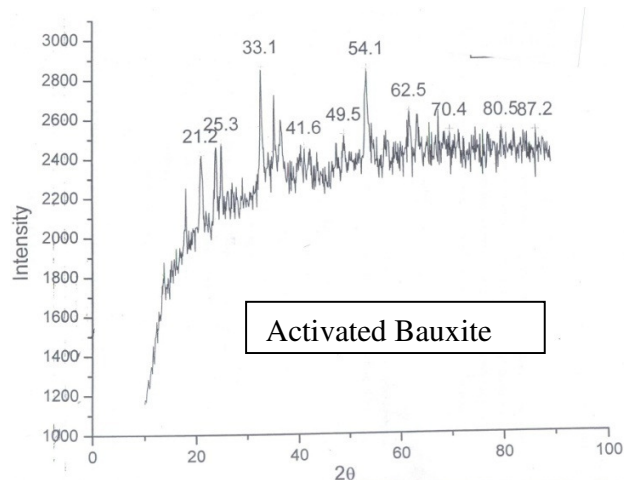

Figure- 1

Activation of Alumina: A method of making activated alumina including the steps of dissolving a double salt of aluminum in a solution of pure water at 85°C., recrystalizing the double salt at a pressure about 250 psi and temperature ranging from 200°C. to 250°C., precipitating out the purified basic double salt, drying the precipitated double salt to drive off water and roasting it at 850°C. to 950°C to drive off the sulfate, washing to remove the potassium sulfate and then drying the remaining alumina to yield activated alumina for use as a high-grade catalyst. A method for producing activated alumina suitable for use as a catalyst, comprising the steps of: (a) dissolving a double salt of aluminum potassium sulfate $Al_2 K_2 (SO_4)_4$ in a solution; (b) heating and pressurizing the resulting solution in a pressure vessel to crystallize and precipitate out a crystal material from said solution; (c) drying and calcining said crystal material to produce a combination of alumina and potassium sulfate; (d) washing with water to remove said potassium sulfate from said combination of alumina and potassium sulfate; (e) drying said alumina remaining after the step of washing to produce an activated alumina.
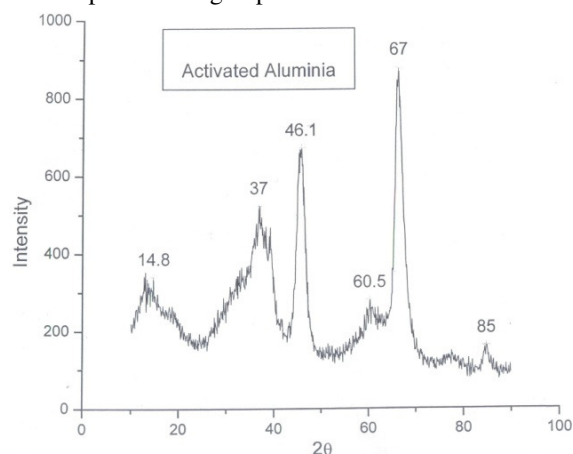

Figure- 2

(b) Activation of rice husk: Active rice husk ash is produced by a method which includes placing a hollow platform having many holes of a size too small for rice husk to enter on an enclosed floor slab, erecting a chimney on the hollow platform in communication with the interior of the hollow platform, forming a cone of rice husk around the chimney to completely cover the hollow platform, igniting the rice husk at the small holes for smolderingly incinerating the rice husk into carbonized rice husk, and allowing the carbonized rice husk to self-burn into ash. Another method of producing active rice husk ash comprising the steps of connecting downstream and upstream rotary kilns in tandem, heating the upstream rotary kiln to a controlled temperature for carbonizing rice husk, heating the downstream rotary kiln to a controlled temperature for burning rice husk into ash, wherein the upstream rotary kiln is heated to a temperature of 300°C-400°C. and the downstream rotary kiln is heated to a temperature of about 600°C.

Table- 4
Physical Properties of Activated Natural adsorbent

Properties	Activated alumina	Activated bauxite	Activated rice husk
Surface area	190	95	102
Pore volume	0.65	0.21	0.34
Bulk density	0.5	0.3	0.8
Size & form	1/16" diameter	Powder form	Powder form

Various Adsorption Isotherms and Theories: (a) Langmuir Isotherm: Langmuir isotherm is based on the assumption that points of valence exist 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 follows:

$$q_e = Q_o b CHPG_e/(1+bC_e)$$

Where q_e is the amount adsorbed. (mg/g), C_e is the equilibrium concentration of adsorbate (mg/l). Q_0 and b is the Langmuir constants related to the capacity and energy of adsorption respectively. The linear form of the Langmuir isotherm can be expressed as

$$1/q_e = 1/Q_o + 1/bQ_o \quad 1/C_e$$

When $1/q_e$ is plotted against $1/C_e$, a straight with slope $1/bQ_o$ is obtained which shows the adsorption follow the Langmuir isotherm. The Langmuir constants b and Q_o are calculated from the slope and intercept with Y- axis. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, r that describes the type of isotherm and is defined by

$$R=1/(1+bC_o)$$

Where b and C_0 are the terms appearing in the Langmuir isotherm. The parameter indicates the shape of the isotherm accordingly.

Table -5

Value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

(b) Freundlich Isotherm: One other equation for isothermal adsorption, the Freundlich or Van Bemmelen equation has been widely used for many years. This equation was based on the assumption that the adsorbent had a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm. The Freundlich equation has the general form:

$$q_e = kfC_1^{1/n}$$

here kf and n are the constants, and If $1/n < 1$. bond energies increases with surface density $1/n > 1$, bond energies decreases with surface density $1/n = 1$, all surface sites are equivalent Freundlich equation can be put in a useful form by taking log of both

$$\log q_e = \log kf + 1/n \log c_e$$

Thus, a plot of log qe and log C_e should yield a straight line for adsorption data, which follow the Freundlich theory. The values of the constants n and kf can be determined from the plot. The intercept is roughly an indicator of sorption capacity and the slope, 1/n of adsorption capacity.

(c) BET (Brunaur - Emmett - Teller) Isotherm: BET derived an adsorption isotherm based on the assumption that molecules could be adsorbed more than one layer thick on the surface of the adsorbent. Their equation like the Langmuir equation, assumes that the adsorbent surface is composed of uniform, localized sites and that adsorption at site does not affect adsorption at neighboring sites. Moreover, it is assumed that the energy of adsorption holds the first monolayer but that the condensation energy of the adsorbate is responsible for adsorption of successive layers. The BET isotherm equation is commonly written as

$$q_e = (A.CX_m)/(C_s-C)[1+(A-1)C/C_s]$$

Where, q_e = amount of solute adsorbed per unit weight of adsorbent (mg/g) C_s = Saturation concentration of the solute C = Concentration in solution at equilibrium

X_m = amount of solute adsorbed in forming a complete mono-layer (mg/g)

Static study: The experimental setup consists of a 1000 ml beaker placed on a magnetic stirrer. A small 2" X 2" nylon wire mesh pocket to hold activated alumina samples was suspended in to the beaker which gives the required agitation. A pipette was used to pipette out the sample at required time interval.

(a) Calculation for the Freundlich & Langmuir Adsorption isotherm at optimum set of parameters for Activated Alumina Expt. Condition-Temp-29±1°C,pH = 6.5 Vol of Sample = 100ml, Initial Concentration = 5mg/l, Contact time = 1hour, stirring rate = 30rpm

Table – 6

Freundlich Adsorption isotherm For Activated Alumina

Sr.No.	Dose(gm/l)	C_e(mg/l)	q_e(mg/g)
1	0.5	3	0.4
2	1.0	2.45	0.255
3	1.5	1.85	0.21
4	2.0	1.75	0.1625
5	2.5	1.55	0.138
6	3.0	1.5	0.116
7	3.5	1.4	0.102
8	4.0	1.39	0.09
9	4.5	1.38	0.08
10	5.0	1.37	0.0725

Figure-3

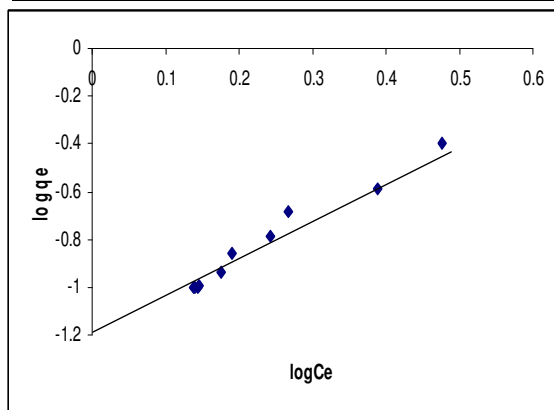$q_e=0.064C_e^{0.485}$ $R^2=0.9262$

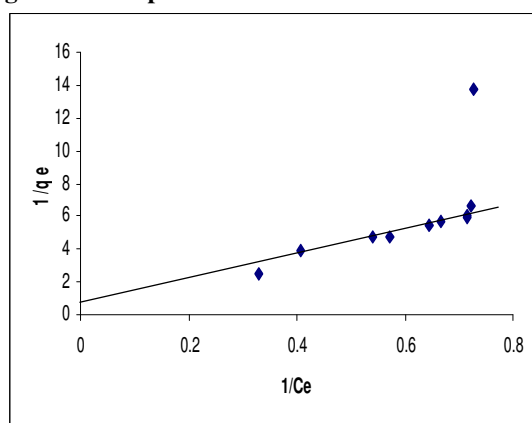**Langmuir Adsorption isotherm For Activated Alumina**

Figure-4

$q_e = 0.156C_e / (1+0.14C_e)$ $R^2=0.986$

(b) Calculation for the Freundlich & Langmuir Adsorption isotherm at optimum set of Parameter for Activated Bauxite. Expt. Condition-Temp29±1°C, pH=6 ,

Volume of sample 100ml, time of contact 1 hour, Initial Concentration 5mg/l

Table- 7

Freundlich adsorption isotherm for Activated Bauxite

Sr. No	Dose (g/100 ml)	C_e (mg/l)	q_e(mg/g)
1	1	1.1	0.39
2	2	0.8	0.21
3	3	0.52	0.149
4	4	0.48	0.113
5	5	0.29	0.0942
6	6	0.27	0.0788
7	7	0.22	0.0682
8	8	0.2	0.06
9	9	0.18	0.0535
10	10	0.17	0.0483

$y = 1.001x - 0.532$
$R^2 = 0.971$
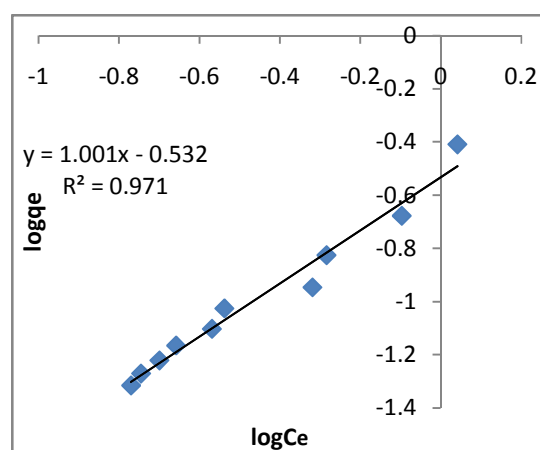
Figure :-5

Langmuir adsorption isotherm for Activated Bauxite.
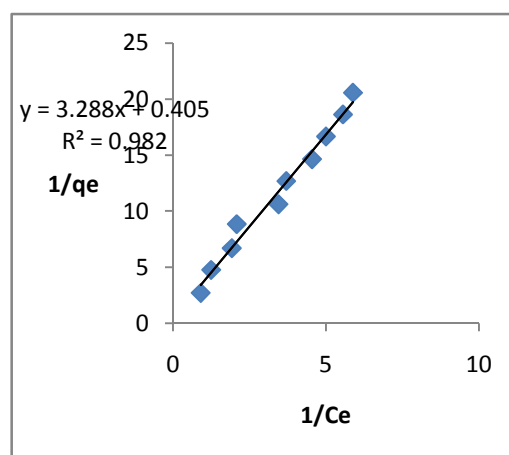

$y = 3.288x + 0.405$
$R^2 = 0.982$

Figure-6

(c) Calculation for the Freundlich and Langmuir Adsorption isotherm at optimum set of Parameter for Activated Rice Husk.

Expt. Condition-Temp-29±1°C pH=2 ,Volume of sample 100ml, stirring rate 40 rpm, dose of adsorbent 10g/l, Contact time =120min

Table-8
Freundlich Adsorption isotherm for Activated Rice Husk

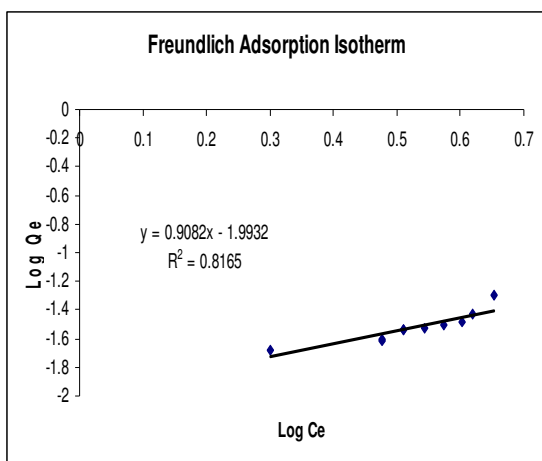| Sr.No.	Dose(gm/l)	Ce(mg/l)	Qe mg/gm
1	1	4.5	0.05
2	2	4.25	0.0375
3	3	4.0	0.033
4	4	3.75	0.03125
5	5	3.5	0.03
6	6	3.25	0.0291
7	7	3.25	0.0291
8	8	3	0.025
9	9	3	0.024
10	10	2	0.021

Figure-7
Langmuir Adsorption isotherm for Activated Rice Husk
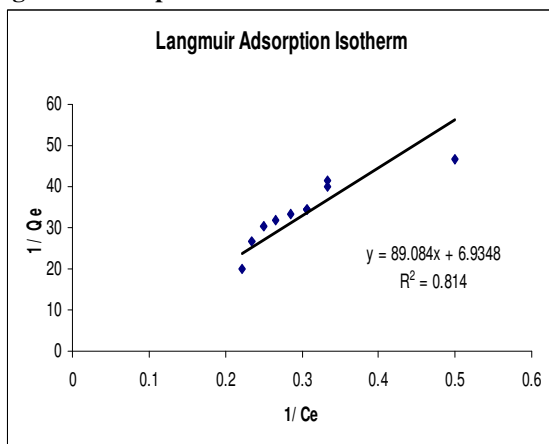

Figure-8
Freundlich constants and exponents for different samples

Table:-9
Langmuir constants and exponents for different samples

S.No	Adsorbent used	Slope 1/n	Equilibrium Constant K_f
1.	Activated Alumina	0.152	0.601
2.	Activated Bauxite	0.965	0.593
3.	Activated Rice Husk	0.659	0.155

Table-10

S. No	Adsorbent used	B	q_m	R_L	R^2
1.	Activated Alumina	0.245	0.476	0.448	0.986
2.	Activated Bauxite	0.382	0.909	0.246	0.982
3.	Activated Rice Husk	0.696	0.978	0.152	0.814

Results and Discussion

Freundlich isotherm is given in the following equation:

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

Where K_f and *n* are Freundlich constants related to adsorption capacity and adsorption intensity, respectively and q_e is the adsorbed fluoride at equilibrium per unit mass of adsorbents (mg/g).
If
1/n < 1, bond energies increases with surface density
1/n > 1, bond energies decreases with surface density
1/n = 1, all surface sites are equivalent
The value of 1/n reported in table 3.2.1are less than 1. so bond energy increases with surface density. **Langmuir isotherm** was plotted with $\frac{1}{q_e}$ Vs $\frac{1}{C_e}$ thus a straight with slope $\frac{1}{Bq_m}$ is obtained which shows the adsorption follow the Langmuir isotherm. The Langmuir constants B and q_m are calculated from the slope and intercept with Y-axis. equilibrium parameter, R_L defined by:

$$R_L = \frac{1}{1 + BC_0}$$

Where *B* is the Langmuir constant and C_0 is the initial absorbate concentration (mg/L), R_L values indicate the type of isotherm to be irreversible (R_L= 0), favorable (0 <R_L< 1), linear (R_L =1) or unfavorable (R_L>1). The Langmuir isotherm was plotted with $\frac{1}{q_e}$ Vs $\frac{1}{C_e}$,as shown in figure 6,7,8 the constant of Langmuir isotherm and the value of R_L are reported in table no 10 and the value are (0 <R_L< 1),so adsorption is favorable.

Conclusions

The percentage of fluoride removal was found to be a function of adsorbent dose and only increase defluoridation efficiency up to a dose of 5 g/100 ml at a given initial solute concentration. Static study was carried out by using natural adsorbents like activated alumina, activated bauxite, activated rice husk. Equilibrium adsorption study was carried out and by Freundlich isotherm it was observed that activated alumina was the best as it gave minimum value of slope (0.152) and equilibrium constant (0.601) as we can see from table no:9 which shows that it is having maximum adsorption capacity. The next adsorbent activated bauxite with slope of 0.965 and equilibrium constant 0.593. This was followed by activated rice husk with slope of 0.659 and equilibrium constant 0.155. So activated alumina is considered as best adsorbent and activated rice husk is inferior adsorbent for this study.

According to Langmuir isotherm the value of R_L is maximum for activated alumina (0.448) than activated bauxite (0.246) and minimum for activated rice husk is (0.152) and also the value of R^2 from table 10 shows the same result as we have studied through the value of langmuir isotherm. So activated alumina is more favorable for this adsorption with respect to activated bauxite and activated rice husk.

Future Scope: Physical Process: The physical activation consists in oxidizing the raw material at high temperature before the presence of an oxidizing agent, usually, water steam. Because this is an endothermic reaction generally, a constant 800°C temperature must be generated. The temperature varies depending on the raw material.

Chemical Process: The chemical activation is based on dehydrating the raw material using chemical substances at an average temperature 400°C to 600°C. This temperature depends on the chemical substance that is used to activate the bauxite. The chemical agents that are generally used are phosphoric acid, zinc chloride and sulfuric acid.

The major oxide contents of this adsorbate are Al_2O_3, SiO_2, F_2O_3, TiO_2 and Na_2O. The Physico-Chemical properties of adsorbents are shown in table.

Table -11
Physico-Chemical properties of adsorbents

Properties	Activated Alumina	Activated Bauxite
Composition, Wt %		
Al_2O_3	93.6	77.7
SiO_2	0.02	10.8
F_2O_3	0.02	6.5
TiO_2	0.002	5
Na_2O	0.35	-
Particle size, mesh	12x32	30x6
Bulck density, Kg/m^3	675	853
Surface area, m^2/g	310	244.08

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