

REMOVAL OF FLUORIDE FROM AQUEOUS SOLUTIONS & SYNTHETIC SOLUTIONS BY VARIOUS ADSORBENTS - REVIEW

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ABSTRACT

This study describes about the various adsorbents that have been used in the aqueous solutions and synthetic solutions to remove the fluoride concentration based on the surface area of the adsorbent. The capacity of the adsorbent depends upon the pH, contact time, initial concentration of the fluoride solution and Temperature etc. The fluoride level must be maintained at certain limits. For drinking purpose the fluoride ion concentration should be less than 1.5 mg/L as per Indian Standards. This review article is mainly aimed at providing precise information about the removal of fluoride in aqueous and synthetic solutions by adsorption technique that have been given by various researchers in the field of fluoride removal. Generally, the fluoride removal has been carried out by membrane and adsorption techniques. This paper deals with adsorption technique in which adsorbent used are titanium hydroxide, amorphous Fe/Al and other mixed hydroxides, algal biosorbent, schwertmannite, synthetic hydroxyapatite, earth oxides, granulated activated carbon and manganese oxides, clays and soils. Recent developments and the adsorption techniques have been clearly discussed.

Key words: adsorptions, pH, temperature, Langmuir, aqueous & synthesis solution.

INTRODUCTION

Fluoride is one of the important heavy metal present in water and waste water. Fluoride ions in water exhibits unique properties, as its optimum dose in drinking water is advantageous to health and excess concentration beyond the prescribed limits affects health (S.Venkata Mohan, 2007). Also Fluoride ions are extremely toxic to human body. A fluoride ion is attracted by positively charged calcium in Teeth and Bones, due to its strong electronegativity. Major health problems caused by fluoride are dental fluorosis, teeth mottling, skeletal fluorosis, and deformation of bones occur in children as well as adults. The waste water also containing high concentration of fluoride ions that may discharged from mines, semiconductor factories, and pharmaceutical companies, which affects the ground water in our earth regions. Due to strict environmental policies, the industries treat the wastewater and the industrial concerns are bound by law to treat waste streams to acceptable discharge standards (Akbar Eskandharpour, 2008).

In India the acceptable range is 1.5 to 10 mg F/L but the limitation of fluoride ions in drinking water is 1.5 mg/L (WHO, 1984) as per WHO, also below 0.5 mg/L is very harmful to human health and formed natural hazards, so treatment of water and waste water is needed. The high concentration of fluoride ions in industrial effluents is controlled by various methods such as adsorption, chemical treatment, ion exchange, membrane separation, electrolytic de-fluoridation, electro dialysis (P.I. Ndiaye, 2005; A.J.Karabelas, 2001; Takaakiwajima, 2009) etc. Among these processes, the adsorption is arguably one of the most promising methods for removal and recovery of fluoride from waste water or water, especially after the precipitation process.

Table 1: Countries affected by fluoride contamination and maximum permissible limits for drinking water

Country	Maximum permissible Limits (mg F/L)	Reference
Japan	15	7,8
Poland	25	7,9
India	10	7,4
Taiwan	15	7,10
China	10	7,11

Theoretically the adsorption of fluoride on to solid particles normally takes three essential steps (Fan et al.)

- I. Diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;
- II. Adsorption of fluoride ions on to particle surfaces;
- III. The adsorbed fluoride ions probably exchange with the structural element inside adsorbed fluoride ions are transferred to the internal surface for porous materials (intra particle diffusion).

There are various types of adsorbents used in this study to remove the fluoride. Each adsorbent having different characteristics and removal of the fluoride contamination is different. Successful and the cost effective removal of contaminants from waste water by adsorption requires optimal operation units. To achieve this, design parameters must be obtained through performance of adsorption equilibrium and in some cases kinetic experiments are used. One such equilibrium data is generated, is a common practice to validate various isotherm models which give the

best description of the experimental results. The frequently tested isotherm models are the Langmuir, two site Langmuir, freundlich, Langmuir- freundlich, redlich- Peterson, toth and Dubini-radushketvich.

Titanium hydroxide derived adsorbents: Wajima et al. investigated the adsorption of Titanium hydroxide for fluoride removal. Titanium hydroxide derived adsorbents was prepared by using titanium oxysulfate $\text{TiOSO}_4 \cdot \text{XH}_2$ (nacalaitesque, japan) as a starting material. It is a gel like adsorbent and the characterization of the adsorbent is same for $\text{TiOSO}_4 \cdot \text{XH}_2$. The mineralogical characteristics of $\text{TiOSO}_4 \cdot \text{XH}_2$ are analyzed by X-ray diffraction (XRD) with a Rigaku RAD -C diffracts meter using $\text{CuK}\alpha$ radiation. Surface morphologies are analyzed by scanning electron microscope (SEM), weight loss and head flows are analyzed by thermogravimetry differential thermal analysis. The surface of the adsorbent is adsorbed by automatic gas adsorption. Using the adsorbent in aqueous solution, the concentration of the fluoride ions is increased initially. The fluoride ions concentration depends upon the pH and contact time. The fluoride ions concentration reached equilibrium value (4.0 mmol/g) within 30 minutes. The mechanism of adsorbent involves ion exchange between Fe^{3+} ions in solution and hydroxyl ion in adsorbent. Generally the adsorbent slurry concentration varying from 0.78 to 15.6 g/l. The amount of fluoride ion on adsorbent, q_f (mmol/g) was calculated using the following equation.

$$q_f = (CF_0 - CF_1) / M \cdot S$$

Where, CF_0 & CF_1 are the concentration of fluoride ions, in aqueous solution at initial and rest time (mg/l)

M is the atomic weight of fluoride

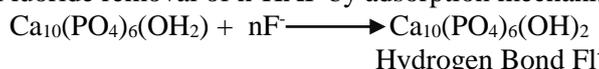
Slurry concentration $S = W / L$.

The surface area of the adsorbent is 96.8 m^2/g . Hence more amounts of fluoride ions are adsorbed. The adsorption is used in real waste water problems. The concentration of fluoride in waste water 1.9 mg/l could be reduced to 0.5 mg/l. The titanium hydroxide adsorbent has high selectivity for F^- compared with other anions and could selectively adsorb fluoride ions in waste water. Equilibrium adsorption capacity is observed in pH 3. The optimum pH range is 3-4. The Equilibrium data were modeled with the help of the Langmuir equation. The overall data were well fitted with Langmuir isotherm model and pseudo first order kinetics obtained using linear adsorption of fluoride on the adsorbent.

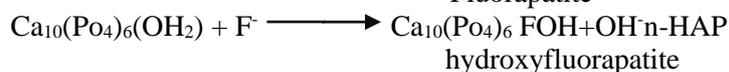
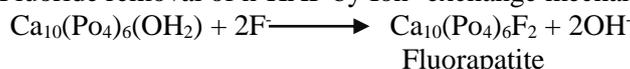
Biosorption on to algal biosorbent spirogyra sp IO₂: Venkata Mohan et al. (2007) studied the biosorption of fluoride pollutants. Generally Biosorbent materials remove various pollutants. Biosorbent materials can be positively bound with large amount of the metals (or) organic pollutants and the phenomena is commonly referred to as Biosorption (APHA, 2008; A.A. Yam, 1985; M. Tsezos, 1982). The biomass is used in the form of the particles. The size of the particles may range from 1-2 mm. The algal spirogyra SP -IO₂ is most suitable for the batch adsorption experiments. In the batch experiments various methods were performed but mostly bottle point method is prescribed for removal of fluoride ions in aqueous solution. 1 gm of adsorbent is mixed with 5% concentration of fluoride ions solutions at 30°C and the pH value is 2. The high amount of fluoride ions should be removed by this technique. The efficiency of F^- ion is 65% at which the contact time is 120 minutes. The residual fluoride concentration is analyzed by Colorimetrically SPHDNS method on a UV spectrophotometer. Fourier transforms infrared (FTIR) scanning electron microscopes are employed to analyse the F^- concentration. Specific surface area of the acid treated biosorbent is 0.154 m^2/g . The adsorbent is having good texture and morphology. Intra particle diffusion models are generated using suitable equilibrium data and develop the Langmuir adsorption model and freundlich model. The pH and temperature is most important in this adsorption study.

Synthesis of n-hap as adsorbent: Sairam et al. (2008) reported that the Nano hydroxyapatite (n-HAP) is cost effective adsorbent to remove the fluoride in aqueous solution. The synthesis of n-HAP involves the reaction of calcium hydroxide and orthophosphoric acid with a Ca/P ratio closed to 1.67. pH level of the reaction should be maintained at 7.5. Otherwise it should be change to calcium monophosphate and calcium hydrates. The level of pH should be maintained by the addition of NH_4 solution. The final form (n-HAP) is a Nano scale of powder $(\text{Ca}_{10}\text{PO}_4(\text{OH})_2)$. The size of powder form is about 200nm with cylindrical rod like shape. The maximum dosage of adsorbent is 0.25g with pH range between 3 to 11. The amounts of F^- ions are measured in various contact time and different pH values. Effective contact time is 30 minutes. The F^- removal followed by different mechanism.

(i) Fluoride removal of n-HAP by adsorption mechanism.



(ii) Fluoride removal of n-HAP by Ion- exchange mechanism.



This adsorbent is mainly used in Thermo dynamic investigation.

Mixed rare earth oxides as adsorbents: Raichurg et al., (2001) studied and reported that a new adsorbent mixed rare earth oxide was effective for removal of fluoride from synthetic solution. They show that hydrates of rare earth oxides remove anions such as Fluoride and lanthanum impregnated silica gel, La(III) and Y(III) impregnated alumina and aluminum impregnated carbon have been used for adsorption of fluoride successfully.

The kinetics of adsorption of fluoride onto rare earth oxides was found to be very rapid in which adsorption took place in just 5-10 min. The adsorption followed the Langmuir adsorption isotherm model. The adsorbent was found to load as high as 12.5 mg of fluoride per gram adsorbent. The optimum pH was found about 6.5 for fluoride adsorption which makes it suitable for use in drinking water treatment. Other ions such as sulphate and nitrate up to 100 mg/l do not greatly affect the adsorption of fluoride there by its dilution of rare earth oxide as selective adsorbent for fluoride. Fluoride easily desorbed at pH 12 having that the adsorbent can be reused. However, the adsorption efficiency of the adsorbent decreased from 98 to 91% after the first regeneration.

Low cost materials as adsorbent: Fan et al., (2002) investigated that the fluoride adsorption behavior of low cost materials and their affectivity of fluoride removal from aqueous solutions at a relatively low level. The adsorption was mainly done with low cost materials such as hydroxyapatite, fluor spar, calcite and quartz under static and shaken condition. At static conditions, the adsorption of fluoride onto solids was a very slow procedure and there was no significant difference between hydroxyapatite and other selected adsorbents within the 10 min, only about 3-6% of fluoride was adsorbed and increased about 2% in 100 min.

Under shaken conditions the selected adsorbents removed fluoride in the solutions. The adsorption of fluoride was controlled by the adsorbent structure and chemical properties and followed the pseudo second order equation. Among the selected materials, the uptake of fluoride was a surface adsorption procedure on calcite, quartz and fluor spar ion exchange procedure on hydroxyapatite. Hydroxyapatite has the highest fluoride adsorption capacity. The fluoride was first adsorbed onto hydroxyapatite surface and then exchanged with OH groups inside the particles. Fluor spar can remove about 25% of fluoride and is only better than quartz. The activation of ferric ions and quartz can significantly improve the adsorption capacity of quartz. After the activation, the fluoride removal increased from 5.6% to 20%. Ferric ion was adsorbed on quartz surface and acted as a bridge between quartz and fluoride.

Calcined Zn/Al hydrotalcite (htlc) as adsorbents: Dipti et al. (2003) studied the use of Zn/Al oxide obtained by thermal decomposition of its HTLC precursor as an adsorbent toward the removal of fluoride from aqueous solutions in the presence of sulphate and phosphate. The adsorption experiment carried out as a function of time, pH, concentration of adsorbate, adsorbent dose, temperature etc. It was found that the maximum adsorption takes place within 4h at the pH is 6.0. The percentage of adsorption increases with increase in the adsorbent dose, but decreases with increase in the adsorbent concentration.

This process involves reaction between fluoride and Dye Lake. During this process, fluoride dissociates a part of the dye lake forming a colorless anionic complex, ZrF_6^{2-} and a dye. The concentration of fluoride ions is inversely proportional to the colour of the solution. The fluoride adsorption increases with increased pH, reaching a maximum at pH 6. At pH 6.0 >85% adsorption takes place. A maximum loading capacity of 13.43 mg/g is obtained at an adsorbent dose of 0.2 g/l, F^- concentration 10 mg/L. pH and temperature is 6 and 30^o C. The surface site becomes less active with increase in the temperature as a result of which the fraction of F^- removal decreases.

Alum impregnated activated alumina as adsorbent: Sushree et al., (2005) investigated the removal of the fluoride from water by the alum-impregnated activated alumina (AIAA) through adsorption. All the experiments are carried out by batch mode. The effect of contact time, pH effect (pH 2-8), adsorption dose (0.5 to 16 g/l), and initial fluoride concentration (1-35 mg/l) had been investigated to determine the adsorption capacity of AIAA. To enhance the adsorption efficacy, the surface of activated alumina was modified by impregnation with alum which has a high fluoride adsorption capacity. The removal tests were carried out by varying contact time, effect of pH, adsorbent dose and initial fluoride concentration.

The removal of fluoride increases with increase in pH up to 6.5 then decreases with increasing pH. The optimum pH was found to be 6.5, which is suitable for the drinkable purpose. Kinetic study that removal of fluoride was found to be very rapid during the initial period i.e. most of the fluoride was removed during 10-60 minutes and reaches to maximum of 92% at 3h. Alum-impregnated active alumina can remove fluoride effectively (up to 0.2 mg/l) from water containing 20 mg/l fluoride. Thus the efficacy of AIAA to remove fluoride from water is found to be 99% at pH 6.5, contact time for 3h, dose 8 g/l. when 20 mg/l of the fluoride is present in 50 ml of water.

Acid treated spent bleaching earth as adsorbent: Mahrananlionglu et al., (2002) studied the adsorption of fluoride from aqueous solution by acid treated spent bleaching earth. Spent bleaching earth (SBE) is a solid waste from edible oil processing industry. SBE has two components: residual oil not removed by filter processing and montmorillonite clay. It has been found that maximum adsorption of fluoride from aqueous solutions takes place at pH value of 3.5. Second order equation was used to describe the adsorption rate of fluoride and adsorption rate constant was calculated. Intra particle and mass transfer coefficients were calculated.

The removal of fluoride aqueous solutions depends on the contact time, pH of the solution and adsorbent concentration. Mechanism studies show that mechanism of fluoride removal on acid treated SBE is complex and both the surface adsorption as well as intra particle diffusion contributes to the rate determining step. The presence of other anions affects the uptake of fluoride. But the cost of acid treated SBE may be slightly higher than some cheap adsorbents.

Chitin, chitosan and lanthanum- modified chitosan as adsorbent: Sanjay et al., (2006) reported that chitin and its materials are effective as an adsorbent to remove the fluoride from drinking water. Chitin, chitosan and 20% lanthanum incorporated chitosan (20% la- chitosan) are used as adsorbents for the removal of excess fluoride from drinking water. It was observed that the uptake fluoride was maximum at original pH (pH 6.7). Chitin is an interesting adsorbent polysaccharide, found in a wide range of organism including bacteria and fungi, but commercially most commonly extracted from shellfish processing waste. Chitosan is a copolymer of 2 – gluosamine and nacetyls -2- gluessamine, derived from chitin, by deacetylating reaction in hot alkali.

The adsorption capacity can be enhanced by spreading chitosan on physical supports that can increase the accessibility of the adsorbate – binding sites. The adsorption of fluoride on the surface of the adsorbent is found to depend mainly on the pH of the solution as well as the concentration and type of co-anions. The adsorption of fluoride at acidic pH (pH5) was high as compared to alkaline (pH). The rate of the adsorption was rapid and maximum fluoride uptake was attained within 20 min. they found that fluoride removal is complex and both the surface adsorption as well as intra particle diffusion contributes to the rate determining step. The percentage removal fluoride in distilled water was higher than field water. This may be because better contains different types of ions.

Schwertmannite as adsorbent: Eskandarpour et al., (2008) reported that schwertmannite adsorbent used in low pH aqueous solution. Schwertmannite adsorbent is stable in low pH and has magnetic properties. It is a synthesized material and probable formula is $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$. If used in powdered form, it can easily and simply be separated using the external magnetic field and thus the adsorbent can easily be reused. It has also been shown to have strong affinity for chromate and arsenate anions. Equilibrium data is a backbone in every adsorbent process. Schwertmannite adsorbent effectively removes the fluoride ions in low pH aqueous solution. Mostly the adsorbent is studied in batch experiment method. The fluoride concentration removal depends upon the pH, temperature, contact time, concentration of fluoride ion solution and different contact time. The amount of schwertmannite adsorbents is 0.05. It's an optimum dose value in 50 ml of 10 ml solution of fluoride ion solution. The pH range is 3-11. The ability of schwertmannite to reduce fluoride to acceptable level at pH is 3.8 was tested by varying the amount of adsorbent dosage in aqueous solution. The effect of co-existing ions was explored at pH 3.8 in binary components adsorption. The ions were chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) to obtain data for fluoride sorption at equilibrium in F/CL-, F/ NO_3^- and F/ PO_4^{3-} binary component systems. The adsorbent is an iron oxide hydroxide material with a poorly crystalline structure, high specific surface area ($162\text{m}^2/\text{g}$) and is brownish yellow colour. Width and thickness of the adsorbent is 2-4 nm and length is 60-90nm(8). If the concentration of temperature range is 30°C to 60°C , 60% of fluoride ions are removed. The Langmuir, freundlich isotherm models are developed using with adsorbent. The adsorbent should be reused after the process of fluoride ions removal. The adsorbent frequently tested isotherm models are the Langmuir, two site Langmuir, freundlich, Langmuir- freundlich, redlich- Peterson, toth and dubini-radushketvich.

Amorphous Fe/Al mixed hydroxides: Sujana et al., (2009) was reported the effectiveness of amorphous iron and aluminum mixed hydroxides in removing fluoride from aqueous solution. A series of mixed Fe/Al samples were prepared at room temperature by co precipitating Fe and Al mixed at pH 7.5. The adsorbent having high specific area is $268\text{m}^2\text{g}^{-1}$. The adsorbent characteristics are conformed by XRD pattern. Batch adsorption studies for fluoride removal on these materials shows that adsorption capacities of the materials were highly influenced by solution pH, temperature and initial fluoride concentration. The optimum pH range is 4-5 instead of pH 5 and more amount of fluoride is adsorbed. The adsorption capacity of the adsorbent is 91.7 mg/g and effective contact time is 2 hours. As adsorption process is associated with several thermodynamics parameters, the temperature dependence was studied in the range of 30°C to 60°C . Initial fluoride concentration is $10\text{-}90\text{mg/L}$. The adsorbent was involved in Langmuir isotherm and to develop the model. The adsorbent is effective in removal of fluoride.

Activated titanium rich bauxite as adsorbent: Nigamananda et al., (2005) investigated the potential of thermally activated titanium rich bauxite (TRB) for the adsorptive removal of excess fluoride from drinking water. Adsorption with respect to various pH, adsorbent dosage, initial fluoride concentration, pressure of influencing ions and heat treatment were investigated by batch equilibrium experiments. Bauxite ore from India are used for this process. It mainly consists of oxide/oxy hydroxides of Ti and Al along small amount of Fe and Si.

The optimum temperature of thermal activation for maximum adsorption capacity is found in between 300°C and 450°C . The optimum pH for maximum uptake is found in between 5.5 and 6.5. The maximum adsorption capacity is found to be 3.8 mg/g at pH 6 with adsorbent dose and initial fluoride concentration of 1g/L to 10 mg/L. Adsorption of fluoride are fairly rapid in first 10 to 15 min and thereafter increases slowly to reach equilibrium in about 1 to 1.5

hours. The adsorption followed a first order kinetics and the data fitted reasonably well to Langmuir and Freundlich isotherm models. The adsorption of fluorides is not greatly affected by the presence of common interfacing ions indicating selectivity of the material towards fluoride adsorption. Competitive effect of interfering ion may be minimized by proper selection of operating pH and fluoride can be removed to the desired level (<1.5 mg/L) from contaminated water using appropriate dose of activated bauxite.

Activated carbon coated with manganese oxides as adsorbents: Yue et al., (2009) investigated the defluoridation potential of a new adsorbent manganese-oxide-coated granular activated carbon (GAC) was coated with manganese oxides to enhance its ability to adsorb fluoride from an aqueous solution. Compared with plain GAC, the fluoride adsorption capacity of this new adsorbent was improved and at least three times greater than that of uncoated GAC. The surface characteristics of coated GAC were observed with scanning electron microscope.

The adsorbent was prepared by coating activated carbon with manganese oxide through a redox process. In the adsorption experiments, 0.5 g GAC – MnO₂ with different amounts of MnO₂ was induced into Teflon bottles to which 100 ml of fluoride solution containing varying concentrations (3-35 mg/l) at pH 5.2 was added. The rate of sorption onto a solid surface is determined by many parameters e.g. the initial concentration of the solute, the structural properties of the sorbent etc. The adsorption kinetics of fluoride onto solid particles is controlled by different mechanisms (a) external mass transfer (b) adsorption of fluoride ions onto particle surface, and (c) intra particle diffusion. Fluoride adsorption on to GAC-MnO₂ follows the pseudo- second order kinetics pattern. The adsorption equilibrium data agree with freundlich isotherms in the tested concentration and temperature ranges. The modified carbon is capable of maintaining a high adsorption capacity over an acidic pH range. Hence it is useful in treating polluted water at low P^H.

Adsorbent	Type of water	pH Range	Concentration	Surface area	Temperature	Model used for adsorption
			(mg l ⁻¹)	(m ² g ⁻¹)	(°C)	
Titanium hydroxide	aqueous solution	3 to 4	0 to 200	96.8	25	Langmuir & Freundlich
Amorphous Fe/Al & Mixed hydroxides	aqueous solution	5.00	10 to 90	268	40 to 60	Langmuir
Algal Biosorbent Spirogyra sp-IO2	aqueous solution	2.00	–	0.154	30	Langmuir
Mixed rare earth oxides	synthetic solution	6.50	50	6.75	29 ± 1	Langmuir
Schwertmannite	aqueous solution	3.80	10 to 90	162	22 to 40	Langmuir, Freundlich, Redlich-Peterson, Dubinin – radushketvich
Low cost materials	aqueous solution	6.00	3x10 ⁻⁵	0.057	–	Langmuir & Freundlich
Synthetic hydroxyl-apatite at nano scale	drinking water	3 to 11	10	200 nm	30 to 50	Langmuir, Freundlich & Redlich-Peterson
Granular activated carbons Coated & manganese oxides	aqueous solution	5.00	23 to 35	914.17	28 ± 1	Freundlich
Alum impregnated & activated alumina	drinking water	6.50	1 to 35	176	–	Adsorption isotherm (Bradley)
Acid treated spent & bleaching earth	aqueous solution	3.5 to 6.5	5 to 20 mg dm ⁻³	198 to 207	–	Langmuir, DR Isotherm
Chitin, chitosan And lanthanum- modified Chitosan	drinking water	–	6.75	–	30 ± 2	Langmuir & Freundlich
Zn/Al hydrotalcite	aqueous solution	6.00	10	71	30	Langmuir & Vant Hoff
Activated titanium rich bauxite	drinking water	5.5 to 6	52 to 50	30 to 150 µm	27 ± 2	Langmuir & Freundlich

CONCLUSION

A concise explanation of various adsorption techniques for removal of fluoride has been presented. Thus adsorption is a conventional technique, deals with various adsorbents such as: aluminium based materials, calcium based materials, and carbon based materials and certain new materials like rare earth oxides, algal biosorbent, schwertmannite, synthetic hydroxyapatite. The systematic procedure of adsorption for fluoride removal has been presented. Comparison between various adsorbents and its optimum conditions at maximum adsorption had been presented in the form of table for easy reference.

REFERENCES

- A.A.Yam, M.Diouf – Nadiaye, M. Badiane, G.Sawdogo, determination of optimal fluoride dose in Senegal drinking water, *Tech. Sci. Meth.* 90(1995)65-79
- A.J.Karabelas , S.G. Yiantsios, Z. Mettaxiotu, N. Andritsos, A. Akiskalos, G. Acidic charbit,effluents by stavoulias, water and materials recovery from fertilizer industry acidic effluents by membrane process desalin, 138, 2001, 93-102.
- Akbar Eskandharpour, Maurice S. Onyango, AoyiOchieng, Shigeo Asai, Removal of fluoride from aqueous solution at low pH using schwertmannite, *J. Hazard. Mater.*, 152, 2008, 571-579
- APHA, Standard Methods for Examination of Water and Waste Water, 20th ed., American Public Health Association, Washington, Dc 1998.
- B. Grzmil, J. Wronkowskwi, Removal of phosphate and fluorides from industrial waste water, *Desalination*, 189, 2006, 261-268.
- C.Y.Hu, S.L.Lo, W.H.Kuan, Y.D. Lee, Removal of fluoride from semiconductor Waster water by electrocoagulation-flotation, *water res.*, 39, 2005, 895-901.
- F.Shen, X.Chen, P.Gao, G.Chen, Electro chemical removal of fluoride ions from industrial waste water, *chem.Eng.Sci.*, 58, 2003, 987-993.
- M. Mohapatra, S.Anand, B.K. Mishra, Dion E.Giles, P.Singh, review of fluoride from drinking water, *J.Env.manage.*, 91, 2009, 67-77.
- M. Tsezos, B. Volesy, Themechanisam of uranium biosorption by *Rhizopus Arrhizus*, *Biotech, Bioeng.*, 24, 285, 1982, 401.
- M.G.Sujana, G.Soma, N.Vasumathi, S.Anand, Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, *J.Fluoride.chem.*, 130, 2009, 749-754.
- M.Yung, T. Hashimoto, N. Hoshio, H. Myoga, Fluoride removal in a fixed bed packed with granular calcite, *water res.* 33, 1999, 3395-3402.
- P.I. Ndiaye, P. Moulin, L.Dominguez, J.C. Millrt, F.Charbit, Removal of fluoride from electronic industrial effluent by RO membrane separation, *desalination*, 173, 2005, 25-32.
- S. Srimurali, A. Pragathi, J.Karthikeyan, A study on removal of fluorides from drinking water by adsorption onto low- cost, *j. Environ. Pollut.*, 99, 1998, 285-289.
- S.Venkata Mohan, S.V. Ramanaiyah , B. Rajakumar, P.N. Sarma , Removal of fluoride from aqueous phase by bio sorption onto algal biosorbent *spirogyra sp.* IO2: sorption mechanism elucidation *J.Hazard.Mater.*, 141, 2007, 465-474.
- Takaakiwajima, YutaUmata, Shuji Narita, Katsuyasugawara, Adsorption behavior of Fluoride ions using a titanium hydroxide- derived adsorbent, *desalination*, 249, 2009, 323-330.
- WHO, International program on chemical safety, Environmental health criteria 36: Fluorides and fluorine, WHO, Geneva 1984.