

Removal of Fluoride by Non-conventional (NLP, PLP, ALP) absorbents

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ABSTRACT

In the present study Neem Leaf Powder (NLP), Peepal Leaf Powder (PLP), Amla Leaf Powder (ALP) was used as absorbent for the removal of fluoride from the solution. NLP, PLP, ALP showed adsorption area and strong affinity toward fluoride. NLP, PLP, ALP was characterized by FTIR, SEM and XRD studies. Adsorption kinetics indicated clearly shows that the percent of fluoride removal increased by increasing adsorbent dose in all cases. Increased adsorbent dosage at fixed F- concentration provided more available active sites and thus increased the extent of fluoride removal. The Langmuir isotherm model could fit the experimental data well. The optimum conditions for fluoride removal were initial concentration: 5.0 mg/L, adsorbent dose: 1gm/50 mL, pH: 2.0, temperature 50°C ± 2°C, contact time: 120 min. and shaking time: 1hr. Increasing order of fluoride adsorption on leaf powders was as follows: ALP > NLP > PLP.

1. Introduction

Millions of people all around the world are crippled and leading vegetative life because of the fluoride contamination. Fluoride is an electronegative element and acts as a strong oxidizing agent in gaseous state [Acharyya S. K.,1993]. Fluoride is naturally available in the earth's crust 0.065% to 0.09% by weight [Brindha K., 2010]. It is extremely reactive and exists as fluoride ion. Fluoride is the 13th most abundant element on earth. Fluoride is an anion F⁻, the reduced form of fluorine (atomic number - 9) when as an ion bonded to another element, having molar mass 18.998g mol⁻¹. The fluorides belong to the halogen group of minerals and are natural constituents of the environment. Fluorides are mainly found in ground water when derived by the solvent action of water on the rocks and the soil of the earth's crust. Fluoride is the most electronegative of all chemical elements and is never encountered in nature in the elemental form. It is seventeenth in the order of frequency of occurrence of the elements. The main sources of fluoride contamination are geological sources which in turn contaminate the drinking water.] [Ayoob S., Gupta A.K., 2006; Ozsvath D.L.,2009] The principal sources of fluorine were drinking water and food such as sea fish, cheese and tea. Fluoride is present in all waters particularly in ground water with higher concentrations. Fluoride is also present mostly in everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so on [Jamode A. and Sapkal V, 2004].

The presence of fluoride in drinking water, within the permissible limits of 1.0 mg/L, is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage are severe cases [Wang S. L., 2009; Hichour M.,2000]. Fluoride in low concentration reduces the incidence of osteoporosis a condition that causes the loss of bone mass and usually occurs

in old age. The high fluoride level in drinking water leads to skeletal and dental fluorosis [Ayoob S., Gupta A.K., 2006].

According to a recent study, 62 million people are affected by various degrees of fluorosis in India. Out of these; 6 million are affected with a dental, skeletal and non-skeletal form of fluorosis and associated health problems [Susheela A. K., 2001]. Fluorine is often called as two-edged sword. The positive side is about 96% of fluoride in the human body is found in bones and teeth. Fluorine is required normally for the mineralization of bones and essential element of dental enamel.

On the negative side, prolonged ingestion of fluoride through drinking water in excess of the daily requirement is associated with dental and skeletal fluorosis [Park K., 2011]. Fluoride combines with sodium and potassium to form monovalent cations such as NaF and KF which are water soluble, and also it forms divalent cations such as CaF₂ and PbF₂ which are generally insoluble. If the Fluoride level increases than the permissible limit, it becomes toxic, its toxicity lies between lead and arsenic [Jain J. K. and Nidhi Gupta, 2013]. World Health Organization (WHO) recommends it in the range of 0.1-0.5ppm. The standard level of fluoride in the United States is between 0.6 and 0.9 ppm, and for India its between 1 and 15ppm. Fluoride is an essential mineral that in permissible guideline level (WHO, 2006) is beneficial to mankind in dental protection and excessive intake led to various disorders and diseases such as crippling skeletal fluorosis, brittle bones, cancer (lung and bladder), infertility in women, brain and hepatitis damage and Alzheimer syndrome [Dobaradaran S., 2008, Guo X.,2003, Mahvi A.,2006] . The fluoride occurs mainly as sellaite (MgF₂), fluorospar (CaF₂), cryolite (Na₃AlF₆) and fluorapatite [3Ca₃(PO₄)₂Ca (F, Cl)]. As fluorospar it is found in sedimentary rocks and as cryolite in igneous rocks [Mohapatra M. S., 2009]. In micromolar level fluoride is useful as it helps in cell proliferation but in higher concentration millimolar concentration it binds with the

functional amino acid group and inhibit the enzyme activity at the various active centers [Trivedi M.H.,2007;] Adamek E.,2005]. In India the fluoride concentration in underground water is higher (1.5–6.5 mg lit⁻¹ WHO,1993), the limit given by the World Health organization (WHO) is 1.5 mg lit⁻¹ for drinking water [WHO,2004].

Removal of fluoride is extremely important for the conservation of the environment. Through the literature it was confirmed that many techniques are available for fluoride removal such as reverse osmosis [Rao et al., 1998], electro dialysis membrane technologies [Amer et al., 2001], coagulation and precipitation.[Saha, 1993]. Adsorption is the main technique used for removal of fluoride in aqueous solution. Predominate use of adsorption is because of low cost, easily available materials, environment friendly.

2. Types of Adsorbents

Various researcher have reported the low cost adsorbent they are Bhatnagar et al., 2011;Kang et al., 2010;Chen et al., 2011;Poinern et al., 2011;Sundaram et al., 2008;Mourabet et al., 2011and many more.

Review of literature reveals that there are various adsorbents which are used for water treatment. Adsorbents are classified into two categories viz. (1) Conventional (Chemical) adsorbents (2) Non- Conventional (Non-chemical) adsorbents.

The most efficient and commonly used example of conventional adsorbents is activated carbon. The reason that activated carbon is such an effective adsorbent material is due to its high surface area, porous structure and high degree of surface activity. Activated carbon is also highly inert, thermally stable and can be used over a broad pH range. Actually these are the basic properties of good adsorbents.

Literature review also supported the above described properties and described various types of adsorbents (chemical, non- chemical, and bio-adsorbents). Despite the advantage of chemical adsorbents, it suffers from a number of drawbacks viz. quite expensive and regeneration cost is not economical.

In present investigation on removal method following materials are used as adsorbents.

- (1)Azadirachta Indica (Neem)– A non conventional adsorbent
- (2)Ficus Religiosa (Peepal) - A non conventional adsorbent
- (3)Embllica Officinalis (Amla) - A non conventional adsorbent

3. Material and methods

3.1Preparation of Leaf Powder (NLP, PLP and ALP): leaves free from diseases were collected from trees. These leaves were washed with water to remove dust and soluble impurities and were allowed to dry at room temperature under shade. 50 µm fractions of powdered leaves were separated and taken as the adsorbent. The powders after being dried for several hours at room temperature were preserved in glass bottles for use as adsorbents.

3.2 Neutralization of the leaf powder (NLP, PLP and ALP):

The NLP, PLP and ALP were found to be acidic in character in its reaction with water. The powder was mixed with water to obtain 1% slurry (1 g NLP, PLP and ALP in 100 mL double distilled water). It was filtered and washed with distilled water to remove acidic contents. The washing was continued till the pH of the filtrate became near neutral, the powder was first dried at room temperature and then in an oven at 60°C to remove moisture. This biomass was stored in air tight glass container to protect it from humidity.

3.3 Determination methods of ions concentration:

Determination of Fluoride (F⁻) ion: JENWAY ion meter and a fluoride selective electrode (JENWAY ISE: 924305) equipped single junction calomel electrode was employed for the measurement of fluoride ion concentration. In each experimental set 25 mL of fluoride sample was taken out and ISA solution was added to adjust pH. The method of direct potentiometer was used, where the concentration can be read directly. The fluoride ion selective electrode was calibrated prior to each experiment in order to determine the slope and intercept of the electrode.

3.4 Characterization of the adsorbent:

Fourier Transform Infrared (FT- IR) spectrum for unloaded and loaded were recorded by using standard KBr diffusion method to obtain the spectrum using Shimadzu – 8400 S in wave number range of 4000 – 500 cm⁻¹. SEM was carried out using (NOVA NANO FEG- SEM 450 with EDAX, Mapping system) at accelerating voltage of 5 KV, spotting - 3.5, working distance - 4.2 mm and magnification range - 350x - 5000x. Powder X-ray diffraction (PXRD) patterns were recorded using benchtop X-ray diffractometer (Model: Rigaku Miniflex 600). The operating target voltage was 30 kV and the current was 15 mA. The radiations of Cu K α were generated using X-ray generator and the β radiations were suppressed using Ni filter. The sample was powdered and scanned for 2 θ ranges from 5° to 80°, with goniometer specification radius of 150 mm and sollar slit $\pm 2.5^\circ$ (divergence angle).

4. Experimental procedures

Batch equilibration method was followed for the optimization process. The adsorption capacity of all types of adsorbents was investigated. In each case a fixed amount (1.0 gm) was placed in a conical flask. An ion(s) solution was then added to each adsorbent and followed Langmuri and Freundlich isotherm.

4.1 A Fourier Transform Infrared:

A Fourier Transform Infrared (FT- IR) spectrum of unloaded and loaded were recorded by using standard KBr diffusion method to obtain the spectrum using Shimadzu – 8400 S in wave number range of 4000 – 500 cm⁻¹. The NLP, PLP and ALP sample was kept in an oven at 60°C for removal of moisture for 3-4 hrs, the sample was cooled to room temperature in desiccators and then, a tiny amount was spread on a nujol film placed between two KBr windows.

Table No. 1: Bands assigned to the surface functional groups of NLP, PLP and ALP before and after adsorption of F-

Sr. No.	NLP, PLP and ALP (before adsorption of F)	NLP, PLP and ALP (after adsorption of F)	Bond stretching
1	3284.88 in case of NLP 3296.46, 3207.73 in case of PLP 3284.88 in case of ALP	3269.45 in case of NLP 3589.65 in case of PLP 3338.89 in case of ALP	-O-H in alcohols, acid, phenols and -N-H in amines and amides.
2	2924.18, 2854.74 in case of NLP, PLP and ALP	2918.40, 2852.81 in case of NLP 2918.40, 2850.88 in case of PLP 2918.40 in case of ALP	-C-H in -CH ₃ and CH ₂ .
3	1722.49 in case of NLP and ALP 1732.13 in case of PLP	1658.84 in case of NLP 1660.77 in case of PLP 1693.56 in case of ALP	-C=O in carbonyl, carboxyl group and lactones.
4	1649.19, 1612.54, 1543.10, 1442.80 in case of NLP and ALP 1545.03, 1429.30 in case of PLP	1543.10 in case of NLP 1539.25 in case of PLP 1450.52 in case of ALP	-C=C- in aromatic rings, -C=O in highly conjugated.
5	1319.35, 1039.67 in case of NLP and ALP 1062.81 in case of PLP	1317.43 in case of PLP 1346.36, 1055.10 in case of ALP	-C-O in alcohols, phenols, ethers, esters, acids, epoxides, lactones and carboxylic anhydrides.
6	879.57, 761.91, 638.46 in case of NLP and ALP 789.62, 686.62, 630.74 in case of PLP	651.96 in case of PLP 883.43, 615.31 in case of ALP	-C-C- deformations and out of plane -C-H deformation in aromatic rings.

The peaks at 3560.71, 3284.88, 3269.45, 3182.65 cm⁻¹ for NLP, 3306.10, 3296.46, 3207.73 cm⁻¹ for PLP and 3524.06, 3338.89, 3294.53, 3284.88 cm⁻¹ for ALP respectively, are the indicator of O-H (free) and N-H groups.

The stretching of -OH groups bound to methyl group radicals presented in fig.1 and 2 is 2924.18, 2918.40, 2854.74, 2852.40, 2850.88 cm⁻¹ for NLP, 2918.40, 2854.74, 2848.96 cm⁻¹ for PLP and 2928.40, 2924.18, 2854.74 cm⁻¹ for ALP .

The peaks located at 1728.28, 1722.49 cm⁻¹ for NLP, 1737.92, 1732.13 cm⁻¹ for PLP and 1722.49, 1712.85, 1710.92

cm⁻¹ for ALP respectively are the Characteristics of C=O group stretching from aldehyde and ketones.

The appearance of -OH group and C-O groups conforms the presence of carboxylic group in the adsorbents.

Therefore we concluded that the The -OH, -NH, carbonyl. Carboxylic groups are important sorption sites. The FTIR spectrum of NLP, PLP and ALP after adsorption of F- is shown in fig 1 and 2 respectively.

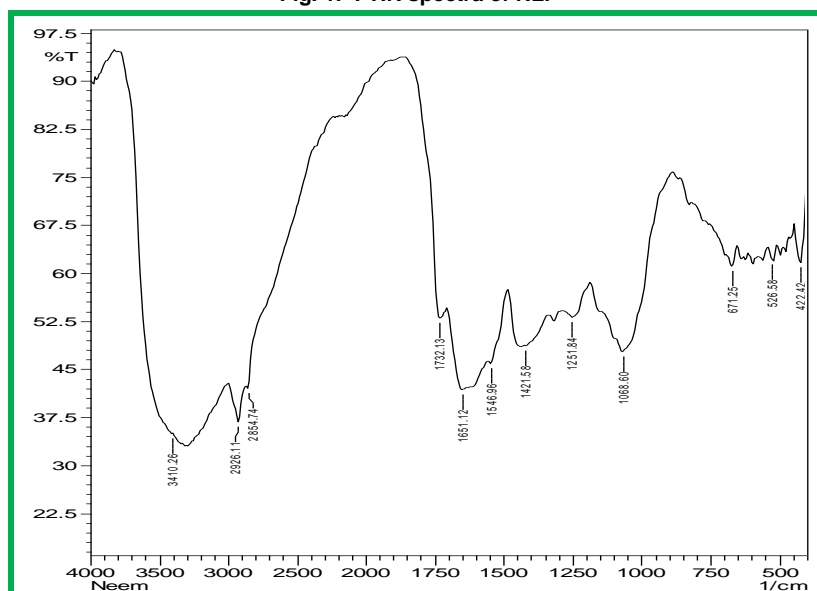
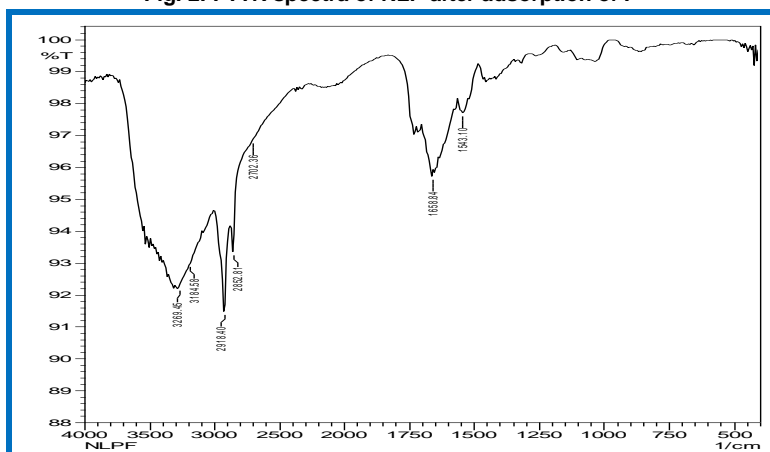
Fig. 1: FTIR spectra of NLP

Fig. 2: FTTR spectra of NLP after adsorption of F-



4.2 SEM Study of Surface Topography:

Surface topography of the NLP, PLP and ALP was observed with Scanning Electron Microscopy (SEM) at the Regional Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Sardar Patel Centre for Science and Technology, Gujarat (India).

The SEM of NLP, PLP and ALP before and after adsorption of F⁻, Pb²⁺ and As^{3+/5+} are given in fig 3, 4 and 5 respectively.

- a) The NLP, PLP and ALP
- b) NLP, PLP and ALP after adsorption of F⁻,

The SEM images of particles loaded with F⁻ is as shown in fig. 3, 4 and 5 respectively. It is evident that active sites of adsorbents are covered due to the adsorption of constituent ions. Fig. 3, 4, and 5 shows progressive changes in the surface particles with native adsorbents which depicts that the constituent ions have deposited as aggregates in the adsorbents.

NLP (Neem Leaf Powder): Fig. 3 shows quite rough texture of surface of the particles with quite big voids throughout the surface. This indicates that particles are having some porosity.

SEM image of the surface of unloaded and loaded NLP

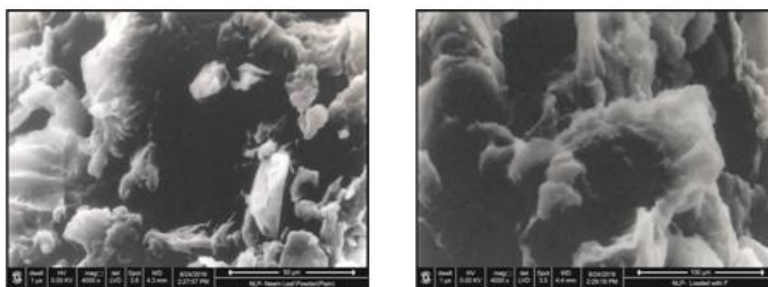


Fig. 3

PLP (Peepal Leaf Powder): The SEM image of PLP-plain as shown in fig. 4 indicates a little smoothness along the surface with a little even texture. It can be seen that adsorption

of F ions does not contribute towards change in surface texture as shown in fig. 4. It is notable that surface look still smooth as compare to that of NLP.

SEM image of the surface of unloaded and loaded PLP

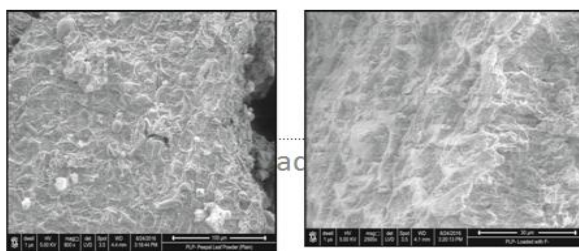


Fig. 4

SEM image of the surface of unloaded and loaded ALP

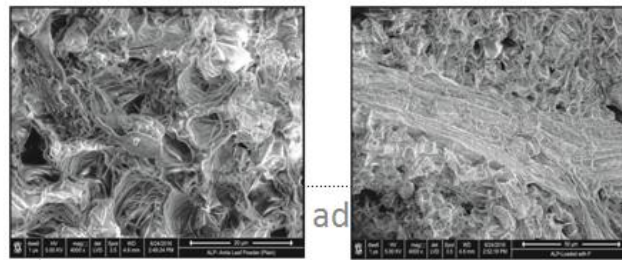


Fig 5

ALP (Amla Leaf Powder): The SEM image of ALP - plain passes almost the same texture as that of PLP; however this sample has a little more roughness which is clearly visible fig.

5. After the adsorption of F⁻ ions fig. 5 it can be seen that these ions are well distributed at adsorption sites and do not cause any observable change.

XRD

Fig. 6: Comparison of unloaded adsorbents

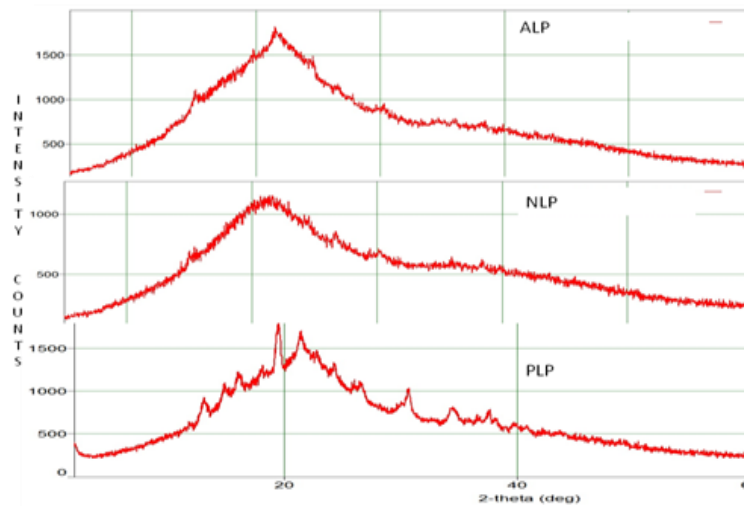


Fig. 7: XRD pattern after the adsorption of F⁻ on NLP

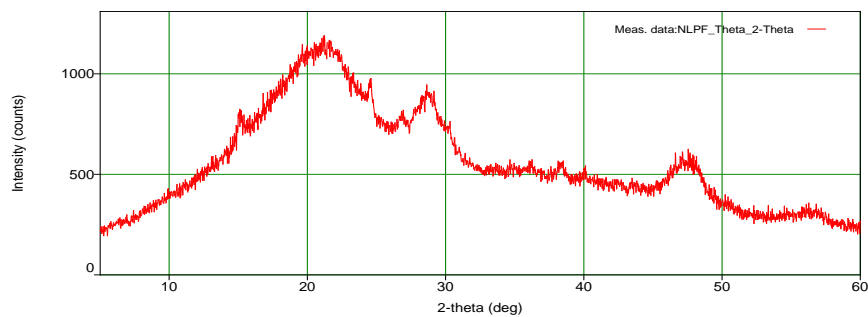


Fig. 8: XRD pattern after the adsorption of F⁻ on PLP

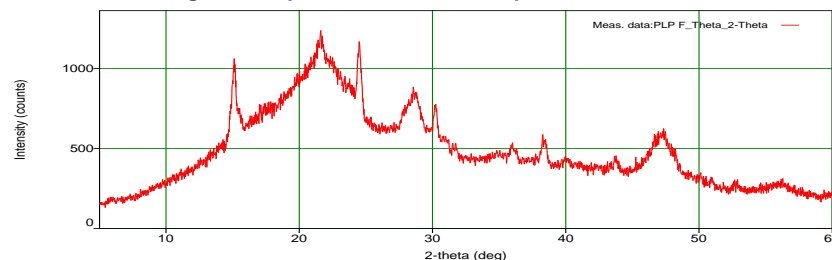


Fig. 9: XRD pattern after the adsorption of F⁻ on ALP

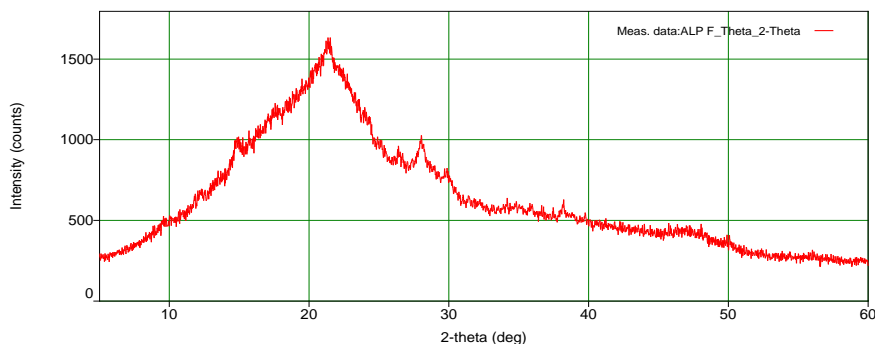


Fig. 6 depicts the X-ray diffraction patterns of the leaf powders. A perusal of these patterns indicates the amorphous character with a broad peak centered on 20°, which is characteristic of polysaccharides (cellulose, starch, etc.). However, PLP exhibited several crystalline peaks. The adsorption capacity was found to be of the order NLP > ALP > PLP. It can be inferred that the crystalline or ordered structure prevents adsorption of ions into the deeper layers, whereas amorphous structures allows penetration of ions into the

adsorbent. For ALP these peaks appeared as doublets, indicating interaction with functional groups also besides the crystallization over the surface.

In conclusion an amorphous nature of the resultant material in XRD study indicated a fast adsorption due to stronger adsorption capacity, whereas crystalline structure indicated slow adsorption

Table No.2: Removal of toxic ions

The adsorption batch experiment was conducted under the following condition

S. No.	Various conditions applied during batch experiment	
1.	Adsorbate	Fluoride solution [0.1-0.5 mg/L]
2.	Adsorbents	(1) NLP (2) PLP (3) ALP
	pH	6.5
3.	Adsorbent dose	0.2 gm, 0.4 gm, 0.6 gm, 0.8 gm, 1.0 gm
4.	Contact time	30 min., 60 min., 90 min., 120 min., 150 min., 180 min
5.	Temperature	20° ± 2°C, 30° ± 2°C, 40° ± 2°C, 50° ± 2°C
6.	Shaking time	1 hour
7.	Apparatus for determination of F ⁻ concentration	JENWAY Ion meter and JENWAY ISE - 924305 with single junction calomel electrode

5. Factors affecting adsorption

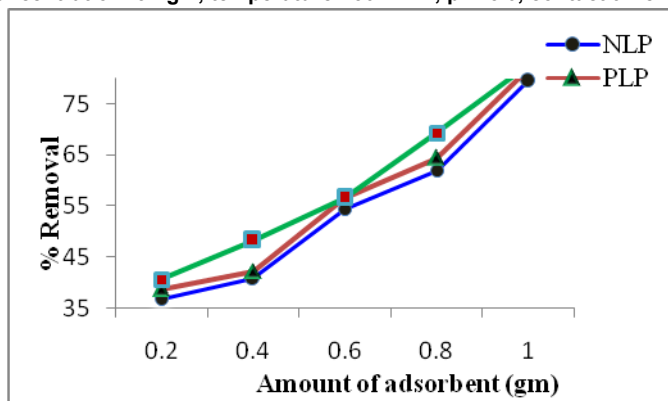
There are many factors which affect the adsorption of the NLP, PLP, ALP and these factors are discussed along with the result:

5.1. Effect of adsorbent dose: The effect of NLP, PLP and ALP dosage on fluoride removal was studied, using 0.2-1.0 gm at initial fluoride concentration: 5mg/L, temperature: 30° ± 2°C, pH: 5.0, contact time: 2hr., shaking time: 1hr. Contact time was ended before reaching equilibrium. The results are depicted in figure 10. It is clearly understood from

the graph that the percent of fluoride removal increased by increasing adsorbent dose in all cases.

Adsorption increases up to 79.49% with adsorption dose of 1gm/50mL in case of NLP, up to 81.89% with adsorption dose of 1gm/50mL in case of PLP, up to 82.76% with adsorption dose of 1gm/50mL in case of ALP, because increasing adsorbent dosage at fixed F⁻ concentration provided more available active sites and thus increased the extent of fluoride removal. Similar results have been reported by [Karthikeyan and Elango, 2008]. The adsorption capacity for ALP > PLP > NLP.

Fig. 10: Effect of different adsorbent dosage on Fluoride removal by NLP, PLP and ALP
(Conditions: initial concentration: 5mg/L, temperature: 30± 2°C, pH: 5.0, contact time: 2hr, shaking time: 1hr)



5.2. Effect of pH: The removal of an ion by adsorption is highly dependent on pH of the solution which affects the change in surface of adsorbent and the degree of ionisation by speciation of adsorbate. The effect of pH studied at 30°C ±

2°C, initial fluoride concentration: 5mg/L, adsorbent dose: 1gm/50mL, contact time: 2hrs. and shaking time: 1hr. with varying pH.

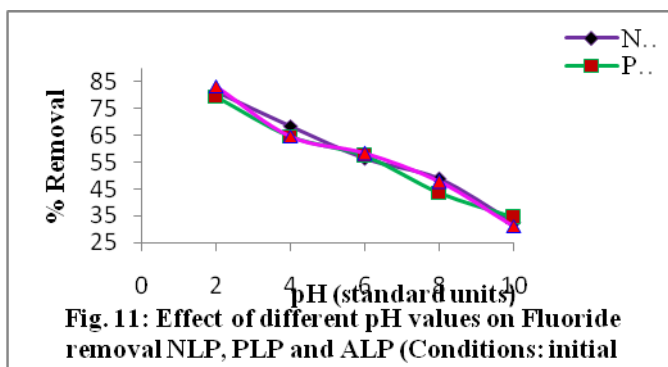
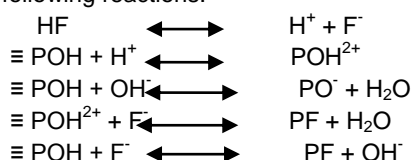


Fig. 11: Effect of different pH values on Fluoride removal NLP, PLP and ALP
(Conditions: initial concentration: 5mg/L, adsorbent dose: 1gm/50mL, temperature: 30°C ± 2°C, contact time: 2hrs. and shaking time: 1hr.)

Figure 11: Effect of varying pH level on Fluoride removal by NLP, PLP and ALP

It is observed from the fig. 11 that with increasing pH of the solution from 2.0 to 12.0 the extent of removal decreases 81.49 to 32.35 in case of NLP, 79.42 to 34.30 in case of PLP, 83.36 to 31.28 in case of ALP. The figure shows that the adsorbed fluoride increased at lower pH in all cases. This behaviour is due to excess of OH⁻ ions which compete effectively with fluoride ions, at higher pH there is a decrease in the amount of fluoride absorbed and which in turn removed from the solution. The surface of the adsorbent gets positively charged which enhances the adsorption of negatively charged fluoride ions through electrostatic force of attraction at lower pH. The results are in good agreement with that reported by [Prasanna, P. Beedkar et al, 2013]. The adsorption capacity of adsorbents at all used pH values were as follows: ALP > NLP > PLP

Fluoride can be adsorbed on the surface of adsorbents by the following reactions:



Where POH, POH²⁺ and PO⁻ are neutral, protonated and deprotonated sites on NLP, PLP and ALP and PF is the active site fluoride complex.

At lower pH, the surface of the NLP, PLP and ALP adsorbents is predominantly positive since more protonation takes place with the adsorbent sites. The fluoride species exist predominantly as HF (pKa = 3.2), which is weakly ionized, thus the removal of fluoride is less. With increase in solution pH the dissociation of the HF increases and the positive charge density of NLP, PLP and ALP adsorbents gradually decreases. However, up to pH 7 it remains predominantly positively charged with some neutral sites, which results in maximum removal of fluoride at lesser pH values. However, above pH 7 the increase in solution pH converts the surface of the NLP, PLP and ALP adsorbents as predominantly negatively charged, fluoride also exists as negatively charged fluoride ion. Thus, the repulsive force between the peepal leaf powder adsorbent and the fluoride reduces chemi-sorption of fluoride at pH greater than 7 and as a result the % removal of fluoride decreases.

5.3. Effect of temperature:

The removal of fluoride from aqueous solution by NLP, PLP and ALP at various temperatures was studied by

conducting batch experiments at $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$, $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$, $40^{\circ}\text{C} \pm 2^{\circ}\text{C}$, $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$ at initial fluoride concentration: 5mg/L, Adsorbent dose: 1gm/50mL, pH: 5.0, Contact time: 2hrs., Shaking time: 1hr. The result is depicted in figure12. The figure shows that fluoride adsorption increased with increase in temperature. NLP shows more adsorption

performance than others at different temperatures. Percentage of fluoride removal at $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$ onto NLP is 94.00%, on PLP is 93.04%, ALP is 86.27% noted. After $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$ the adsorption of fluoride decreases due to the weakened interactive forces. The adsorption capacity for NLP and PLP was higher than ALP at all temperatures.

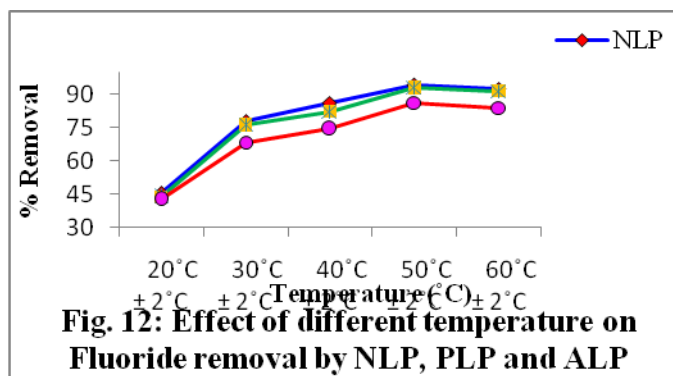


Fig. 12: Effect of different temperature on Fluoride removal by NLP, PLP and ALP (Condition: initial fluoride concentration: 5mg/L, Adsorbent dose: 1gm/50mL, pH: 5.0, Contact time: 2hrs., Shaking time: 1hr.)
 Figure 12: Effect of temperature on fluoride adsorption

5.4. Effect of contact time: The removal of fluoride from aqueous solution by NLP, PLP and ALP at various contact time was studied by conducting batch experiments at initial concentration: 5mg/L, Adsorbent dose: 1gm/50mL, Temperature: $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and shaking time: 1hr. The results are depicted in Figure 13. It is observed from the graph that maximum fluoride removal for NLP is 80.78%, for PLP is

86.76%, and for ALP it is 82.78% respectively. Fluoride removal is fast for the first 120 min. and then it remained constant with increase in contact time. The adsorption capacity for PLP was slightly higher than that of others at all contact times. Similar results were obtained in literature at 120 min. [Prasanna, 2016].

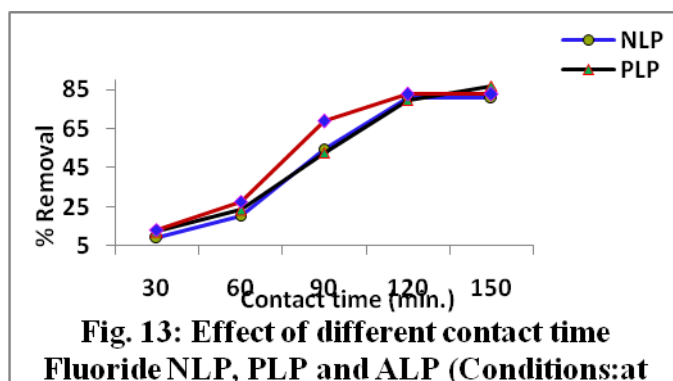


Fig. 13: Effect of different contact time Fluoride NLP, PLP and ALP (Conditions: at initial concentration: 5mg/L, Adsorbent dose: 1gm/50mL, Temperature: $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and Shaking time: 1hr.
 Figure 13: Effect of temperature on fluoride adsorption

5.5. Effect of varying fluoride ion concentration:

The removal of fluoride from aqueous solution by NLP, PLP and ALP at initial fluoride ion concentration was studied by conducting batch experiments at fixed Adsorbent dose: 1gm/50mL, pH: 5.0, Temperature: $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$, contact time: 2hrs. and shaking time: 1hr. The results are depicted in figure 14. It is found that the removal of fluoride increases with increasing concentration of fluoride solution. The figure shows that up to 5mg/L, the percentage fluoride removal was 80.31% for NLP, 82.28% for PLP and 81.32% for ALP, while at higher

concentration the adsorption decreased gradually. The increased removal up to 5mg/L indicates the possibility of the monolayer coverage of fluoride ions as directed in adsorption isotherm. The adsorption capacity for PLP was higher than that of others all used initial concentration.

[Inder Kumar Makhija 2010] also has observed that the adsorption efficiency of ongoing adsorption process is favorable for increased fluoride concentration.

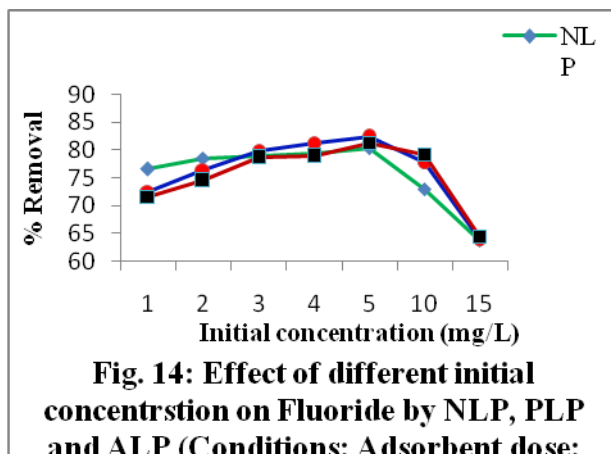


Fig. 14: Effect of different initial concentration on Fluoride by NLP, PLP and ALP (Conditions: Adsorbent dose: 1gm/50mL, pH5.0, Temperature: 30°C ± 2°C, contact time: 2hrs., Shaking time: 1hr.

Figure 14: Effect of varying concentration on fluoride adsorption

6. Adsorption isotherm

Langmuir isotherm equation was studied by plotting $1/C_e$ versus $1/q_e$ and the results are shown in figure 15, 16 and 17. And Freundlich isotherm equation was studied by plotting $\log q_e$ versus $\log C_e$ and the results are shown in figure 18 and 19 respectively. The adsorption isotherm parameters which were calculated from the slope and intercept of the linear plots using the linearized form of the Langmuir (equ-1) and Freundlich (equ-2) together with R^2 values are given in table 3.0

The regression value R^2 indicated that Langmuir model fits the adsorption data and the value of n illustrate the strong attraction between NLP, PLP and ALP with F^- ions. In strict terms the Langmuir isotherm was originally developed for gas phase adsorption, so it is not surprising to see a poor correlation with the experimental results.

Langmuir isotherm:

It assumes a monolayer adsorption onto a uniform adsorbent surface with energetically identical sorption sites [B.Al Duri, 1996;C. H. Giles,1974]. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o \cdot b} \frac{1}{C_e} \dots\dots (1)$$

Where:

C_e = equilibrium concentration of the adsorbate (mg/L)

q_e = amount of adsorbate per unit mass of adsorbent (mg/g)

Q_o and Q_{ob} are Langmuir constants, related to adsorption capacity and rate of adsorption respectively.

Freundlich isotherm

It describes equilibrium on heterogeneous surface and hence does not assume mono layer capacity [B.Al Duri, 1996;C. H. Giles,1974]. The well known logarithmic form of the Freundlich isotherm is given by the following equation followed.

$$\log q_e = \log K_f F + 1/n \log C_e \dots\dots (2)$$

Where:

C_e = equilibrium concentration of the adsorbate (mg/L)

q_e = amount of adsorbate per unit mass of adsorbent (mg/g) K_f and n are the Freundlich constants.

Table 3:

Coefficients for each model equation							
Sr. No.	Isotherm Adsorbents	Langmuir			Freundlich		
		Parameters			Parameters		
1		Q_o (mg/g)	b (L/mg)	R^2	K_f (mg/g)/(mg/L) ^{-1/n}	n	R^2
2	NLP	1000	0.003	0.987	2.667	4.132	0.061
3	PLP	0.589	1.030	0.833	3.265	1.178	0.892
4	ALP	0.624	0.938	0.816	3.133	1.113	0.901

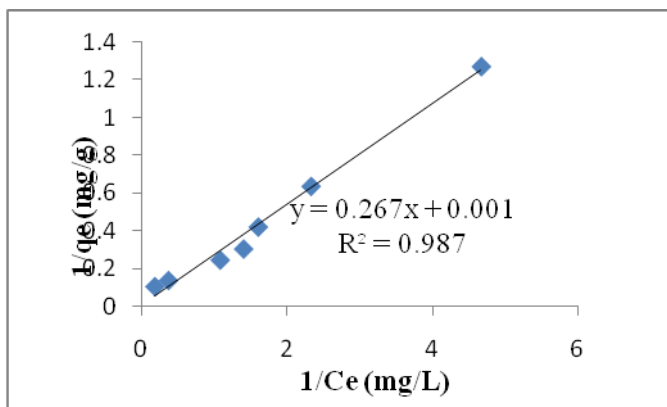


Figure15: Fluoride onto NLP (Langmuir isotherm)

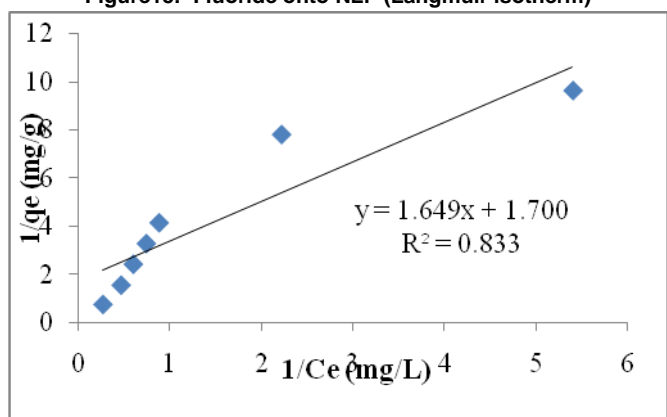


Figure 16: Fluoride onto PLP (Langmuir isotherm)

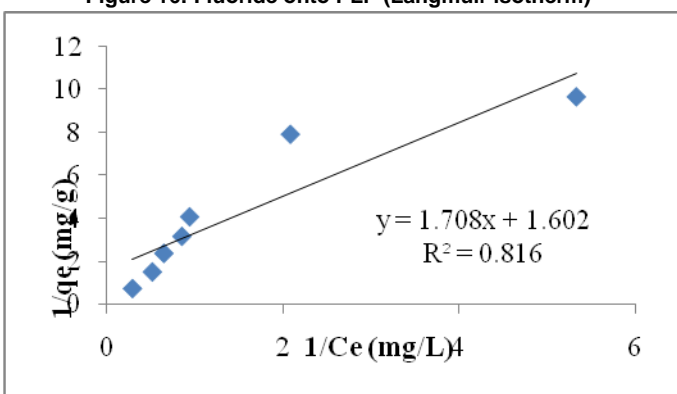


Figure 17: Fluoride onto ALP (Langmuir isotherm)

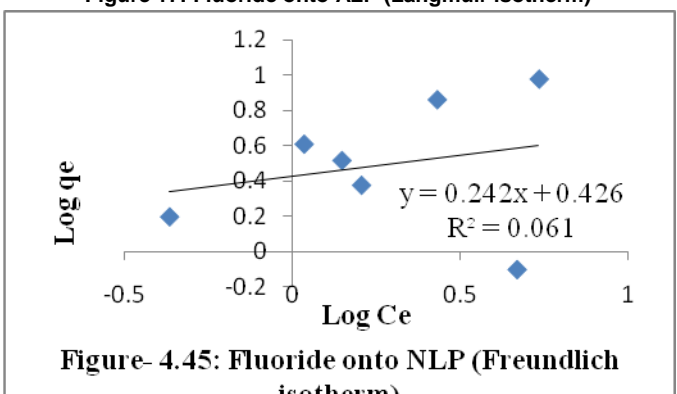


Figure- 4.45: Fluoride onto NLP (Freundlich isotherm)

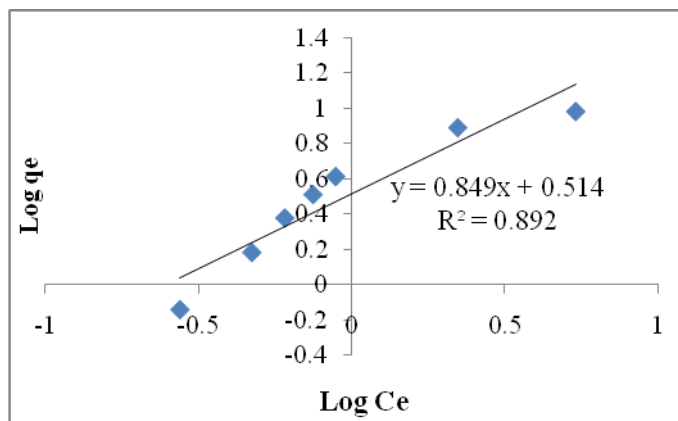


Figure 18: Fluoride onto PLP (Freundlich isotherm)

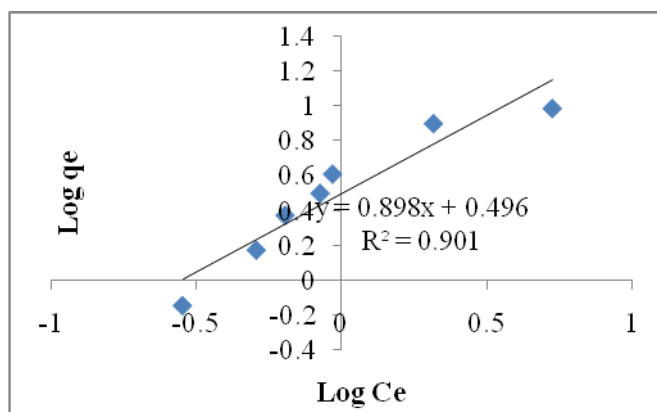


Figure 19: Fluoride onto ALP (Freundlich isotherm)

7. Conclusion

The present study investigated the adsorption of fluoride onto NLP, PLP and ALP. Experiments were carried out at different adsorption parameters (pH, concentration, adsorbent dose and temperature). It was found that the amount of fluoride adsorption increases with the increase of adsorbent concentration which indicates that adsorption depends upon the availability of active sites for fluoride. The highest percentage of fluoride adsorption occurred at the pH: 2.0. The amount of fluoride adsorption increases with the increase of temperature up to 50°C ± 2°C indicates that the adsorption depends upon the availability of active sites for fluoride but the desorption probably took place at about 60°C ± 2°C. The equilibrium of fluoride adsorption was attained in about 120 min. The percentage fluoride adsorption first increased up to 5 mg/L fluoride concentration then after it decreased at higher concentrations. The experimental data of fluoride removal from water confirms the validity of these obtained results and the adsorption data for fluoride onto NLP, PLP and ALP were better correlated to the Langmuir than on the Freundlich isotherm. XRD and SEM study reveals that impregnation with NLP, PLP and ALP with Fluoride is quite well and uniform. The optimum conditions for fluoride removal are initial concentration: 5.0 mg/L, adsorbent dose: 1gm/50 mL, pH: 2.0, temperature 50°C ± 2°C, contact time: 120 min. and shaking time: 1hr. So we concluded that fluoride can be removed satisfactory by leaf powders of (NLP, PLP and ALP) and increasing order of fluoride adsorption by leaf powders is as follows: ALP > NLP > PLP.

References

- Jamode A., Sapkal, V., (2004): Defluoridation of water using inexpensive adsorbents.; J. Indian Ins. Sci.; Vol. 84,5, pp 163-171.
- Susheela, A. K., (2001): "Fluorosis: Indian scienario" A treatise on fluorosis. Fluoro-sis.; Research and Rural Development Foundation; New Delhi, India.
- Mahvi, A. Zazoli, M. Nicpour, B., (2006): Survey of fluoride concentration in drinking water sources and prevalence of DMFT in the 12 years old students in Behshar City. J. Med. Sci. Vol. 6(4), pp 658-661.
- Acharyya, S. K., Lahiri S., Raymahashay B. C., Bhowmik A., (1993) 'Arsenic toxicity of ground water in parts of the Bengal basin in India and Bangladesh: the role of Quarternary stratigraphy and Holocene sealevel fluctuation.; Environ Geol. 39, pp 1127-37.
- Amer, Z., Bariou, B., Mameri, N., Taky, M., Nicolas, S., Elmidaoui, A. (2001): Fluoride removal from brackish water by electrodialysis. Desalination 133, 215-223.
- Duri B. Al., (1996): Adsorption modeling and mass transfer, in G. Mackay, ed., Use of adsorbents for the removal of pollutants from waste waters.; CRC, N.Y pp 133-140.
- Bhatnagar, A., Kumar, E., Sillanpää, M., (2011): Fluoride removal from water by adsorption. Chem. Eng. J. 171, 811-840.
- C. H. Giles, A. P. Silva, I., (1974): A. Easton, A general treatment are classification of the solute adsorption isotherm (II); J. Colloid Int. Sci.; Vol. 47, pp 766-787.
- Chen, N., Zhang, Z., Feng, C., Li, M., Zhu, D., Sugiura, N., (2011): Studies on fluoride adsorption of iron-impregnated granular ceramics from aqueous solution. Mater. Chem. Phys. 125, 293-298.
- Ozsvath D.L., (2009): Fluoride and environment health: a review, Rev. Environ. Sci. Biotechnol. 8 59-79.
- Dobaradaran, S., (2008): Drinking water fluoride and child dental caries in Dashtestan, Iran. Fluoride, Vol. 41(3), pp 220-226.
- Inder Kumar Makhija, Sharma, Indra Prakash Sharma, Khamar, Devang. (2010): Phytochemistry and Pharmacological properties of Ficus religiosa: an overview . Scholars Research Library, Annals of Biological Research. Vol. 1 (4), pp 171-180
- Jain J. K., Nidhi Gupta, (2013): Defluoridation of Water Using Bioadsorbents : Kinetic Study.; IJSR - International journal of scientific research.; Vol. 2 (12), pp 171..
- Brindha K., R., Rajesh, R., Murugan, L., Elango.; (2010): 'Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India'. Environ Monit Assess, 10661-010-1348-0.
- Park K., (2011) Park's Text Book of Preventive and Social Medicine. Ed 21.; Ba-narasidas Bhanot Publishers, 1167. Premnagar, Jabalpur, India, pp 577.
- Kang, J., Song Li B., Yang, J., Zhan, W., Liu, D., (2010). Defluoridation of water using calcined magnesita/pullulan composite. Chem. Eng. J. <http://dx.doi.org/10.1016/j.cej.2010.11.031>.
- Karthikeyan, M., Elango, K. P. (2008): Removal of fluoride from aqueous solution using graphite : A kinetic and thermodynamic study.; Ind. J. Chem. Technol., Vol. 15, pp 525-532.
- Hichour M., Persin F., Sandeaux J., Gavach, C.; (2000): Fluoride removal from waters by Donnan dialysis. Sep. Purif. Technol. Vol. 18, pp 1-11.
- Mohapatra M., S., Anand B. K., Mishra, E.M. Dion Giles, Singh P., (2009): Review of fluoride removal from drinking water.; Journal of Environmental Management.; Vol. 91, pp 67-77.
- Trivedi M.H., Verma R.J., Chinmay N.J., Patel R.S., Sathawara N.G., (2007): 'Effect of high fluoride water on intelligence of school children in India, Fluoride 40 178-183.
- Mourabet, M., El Boujaady, H., El Rhilassi, A., Ramdane, H., Bennani-Ziatni, M., El Hamri, R., Taitai, A., (2011).
- Poinern, G.E.J., Ghosh, M.K., Nga, Y-J., Issa, T.B., Anand, S., Singh, P., (2011). Defluoridation behavior of nanostructured
- Prasanna, Beedkar, P., Kulkarni, Anand, D., Kulkarni, Kavita, S.; Defluoridation of Water by Adsorption Phenomenon of the Powdered Ficus Religiosa in Batch and Continuous Mode.; International Journal of Science and Research (IJSR). (2016), Vol. 5-6, pp 2558-2562.
- Rao, N.V., Mohan, R., Bhaskaran, C.S. (1998). Studies on defluoridation of water. J. Fluorine Chem. 41, 17-24. review on the status and stress effects, Crit. Rev. Environ. Sci. Technol. 36 (2006) 433-487.
- Ayoob S., Gupta A.K., (2009). Fluoride in drinking water: a S. J., Uddin; I. D., Grice; E. Tiralongo Cytotoxic effects of Bangladeshi medicina 'Plant extracts.; Evid Based Complement Alternat Med'
- Wang S. L., Liu C. H., Wang. M. K., Chuang Y. H., Chiang P. N., (2009) Arsenate adsorption by Mg/Al-NO₃ layered double hydroxides with varying the Mg/Al ratio.; Appl. Clay Sci., 43, 79-85.
- Saha, S., (1993). Treatment of aqueous effluent for fluoride removal. Water Res. 27, 1347-1350.
- Sundaram, C.S., Viswanathan, N., Meenakshi, S., (2008). Defluoridation chemistry of synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies. J. Hazard. Mater. 155, 206-215.
- WHO (World Health Organization), (2006) Guidelines for Drinking Water Quality, World Health Organization, Geneva,.
- WHO (World Health Organization), Guidelines for Drinking Water Quality, World Health Organization, Geneva, 1993.
- Guo X. Sun G., Sun Y., (2003): 'Oxidative stress from fluoride induced heap to toxicity in rats, Fluoride., Vol. 36(1), pp 25-29.
- Prasanna, Beedkar, P., Kulkarni, Anand, D., Kulkarni, Kavita, S., (2016): Defluoridation of Water by Adsorption Phenomenon of the Powdered Ficus Religiosa in Batch and Continuous Mode.; International Journal of Science and Research (IJSR); Vol. 5(6), pp 2558-2562.