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Adsorption Analysis, Characterization And Equilibrium Study Of Pigeon Pea Seed Coat (Ppsc) For The Removal Of Fluoride From Ground Water

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Abstract
Fluoride is an essential nutrient for the human body at low concentrations. Fluoride in drinking water can be either beneficial or detrimental to health depending on its concentration. Removal of fluoride from synthetic solution using the peels of Pigeon Pea Seed Coat (PPSC) was studied in a batch experimental analysis. The results of the batch adsorption experiments demonstrated that the maximum fluoride removal was obtained at pH of 6.5. In adsorption Freundlich and Langmuir models were studied and found the best fitted model was Langmuir. The adsorption capacity of PPSC was found on a dose of 3.0 g/L. The adsorption process was exothermic in nature. The parameters are tested and found all within limit of BIS 10500-1991. The effects of coexisting ions were studied. Cost of (PPSC) was analyzed and found very cheap.

Keywords: Defluoridation, adsorption, PPSC, Langmuir & Freundlich Isotherm

INTRODUCTION

Water is an important constituent of our body. It is not only essential for survival but also improves the quality of life. Water is polluted every day by various pollutants or industrial effluents. Fluoride is of the great environmental concern pollutant which contaminates ground water and affects human health. More than 260 million people around the world is affecting by the excess fluoride concentration in groundwater. Only in India, more than 60 million people are at risk of developing fluorosis from fluoride contaminated drinking water (Bhambulkar, A.V. ,2011).
Water is the primary major source of fluoride in daily intake by human beings. The beneficial or detrimental effects of fluoride in water depend on the concentration of fluoride. As per the World Health Organization (WHO), the maximum acceptable limit of fluoride in water is 0.0015 g/L. However, Bureau of India Standards (BIS) has set a limit between 0.0005 and 0.0010 g/L. The acceptable limit varies among countries and lower concentration is recommended for children (Chimote, K., & Bhabhulkar, A. ,2012, March).
Elemental fluoride is more toxic than its oxidized forms and has adverse health effects on human beings as well as on environment. Small concentrations of fluoride in water reduce the incidence of caries, stimulate bone formation and harden the enamel of teeth. When the concentration is beyond the acceptable limit, it causes lesion of the liver, thyroid and endocrine glands, (Sahare et al. ,2019)
dental and skeletal fluorosis, arthritic symptoms and bone fracture well before the onset of crippling fluorosis, etc. De-fluoridation of water is quite difficult and expensive. Various natural and synthetic materials have been applied to solve this world wide problem. Ion-exchange, precipitation (Ganorkar R. A. et al. ,2014), nano-filtration, electro-chemical, reverse osmosis and adsorption are most widely developed techniques methods for de-fluoridation of water. Among them adsorption is quite effective method

because it is easy to operate, needs less space, eco-friendly and cost effective method. Natural, natural modified and synthetic materials have been widely applied as adsorbents for removal of fluoride ions from water.

Plant Description:

- **Plant height**

Short: 2 to 2.5m

- **Flower color**

Yellow

- **Pod color**

bright green

- **Seed color**

Brown, white

- **Seed shape**

Round

Fig.1: Pigeon Pea plant

Source: International Crops Research Institute for the Semi-Arid Tropics

MATERIAL AND METHODS

Different bio-materials were studied and Pigeon Pea Seed Coat (PPSC) are selected for this research study. All used chemicals are AR grades. Stock solution was prepared by diluting the known quantity of NaF in a liter of distilled water. The concentration range of adsorbate test solutions was prepared from the stock solutions varied between 5, 7, and 10 mg/L. Every time fresh solution was prepared for experimentation. pH was adjusted by standard acid and base solutions of 0.1 N HCl and 0.1 N NaOH respectively (Bhambulkar, A. V. & Isha. P.. Khedikar ,2011)

Material

Pigeon Pea Seed Coat (PPSC) was collected from the rural areas of Amravati District, Maharashtra state (India). The collected waste of PPSC was grounded to a fine powder and sieved through the different sieves size. The material was washed, dried and kept it in muffle furnace at 500 ^{0}C temperature for 2 hrs. After removing from muffle furnace sample is again washed by distilled water and dried it again. The developed material used for the experimentation. Removal of fluoride concentration of 10.0 mg/L, dose was observed too much high. Hence the adsorbent was again activated at 700^{0}C and found a 3.0 g/L. This adsorbent dose was used for the further study.

Method of analysis

SPADNS photometric method was used for the determination of fluoride ions, at 570 nm using the double beam UV–vis spectrophotometer (UV–VIS-8500, Tech comp Ltd, Hong Kong). The pH of the solution was measured by using the pH meter of the Elico model (LI613) (Asare et al. ,2019).

CHARACTERIZATION OF ADSORBENT

Table: 1: Chemical Compositions of PPSC

Elements	Percentage
Ca	37.94
Mg	10.67
Fe	0.46
Si	0.33
Al	0.22
Other	49.99

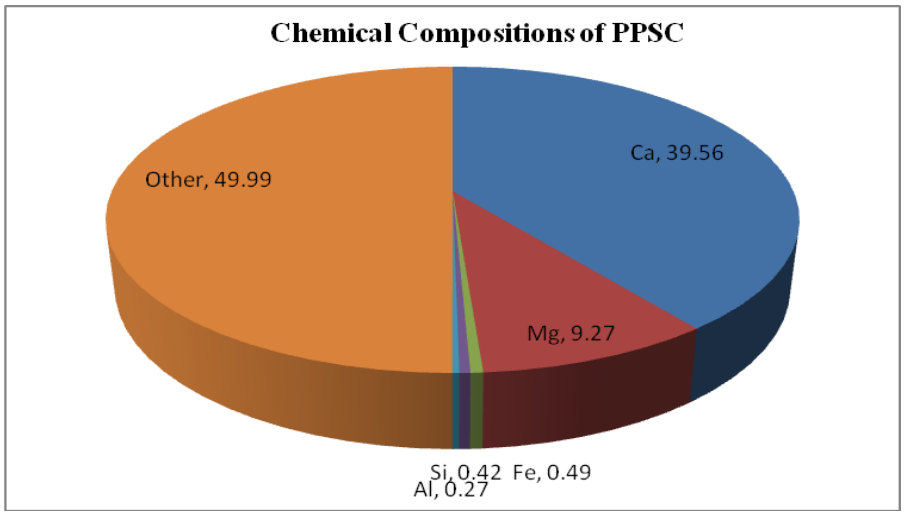

Fig.2: Chemical Compositions of PPSC

X-ray Powder Diffraction (XRD)

In this test samples were scanned for 2ø range from 5 to 60°.The X-ray diffraction spectrum pattern of the PPSC did not show any significant changed in loaded and unloaded PPSC with fluoride. (fig.3), thereby indicating the amorphous nature of the product.

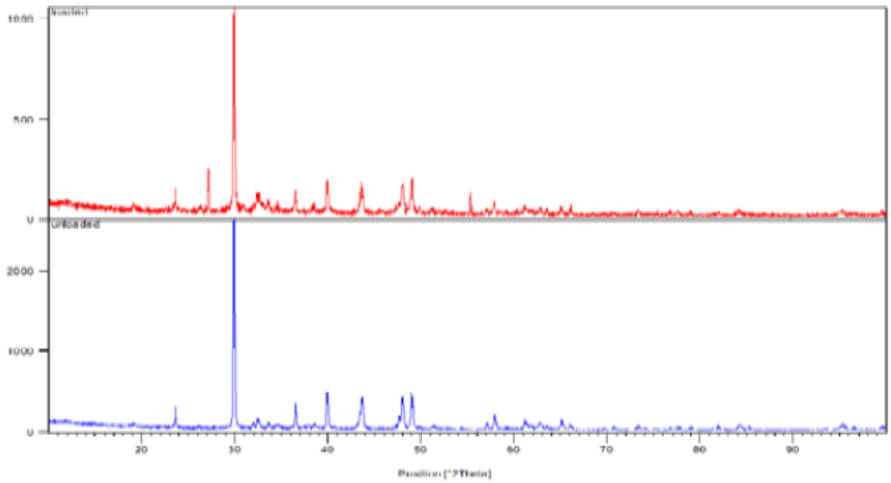

Fig.3: XRD of PPSC (Loaded & Un-loaded)

XRD was performed on the treated Pigeon Pea Seed Coat (PPSC) to predict changes in the crystal structure. Since a few decades ago, one of the most widely used techniques in the modern era for classifying materials and identifying crystals is X-ray diffraction (XRD) examination. PPSC, X-ray diffraction before and after, fluoride ions were adsorbed. Figure 9 shows symmetric, strong peaks in the PPSC before fluoride ion adsorption. The figure below shows the position and kind of peaks that result from the adsorption of fluoride ions, and this peak indicates that the structure is crystalline. No peaks were found to have developed, indicating that the structure is amorphous angles for the samples' scans.

Scanning Electron Microscopy (SEM)

Scanning electrons microscopes analysis was performed to understand the morphology of IPP. From fig.4, it is observed that the openings are enough to remove fluoride from water. From Fig.5, shows the openings are blocked after adsorption of fluoride ions.

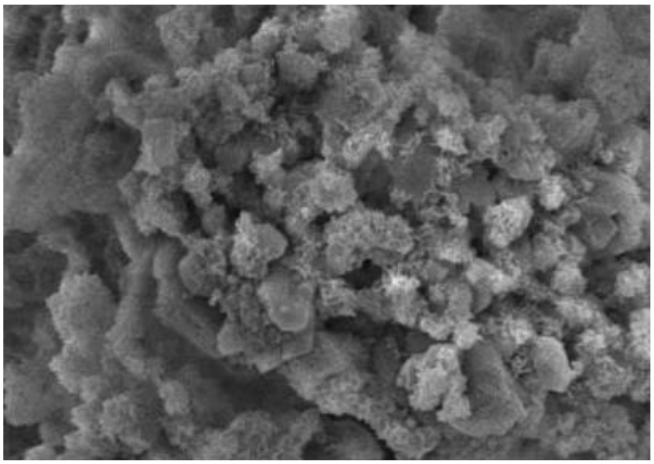

Fig.4: SEM, Loaded image of adsorbent PPSC

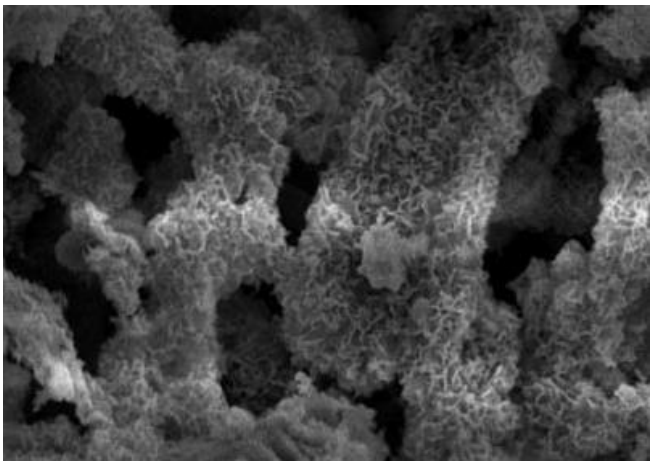

Fig.5: SEM, Unloaded image of adsorbent PPSC

BATCH ADSORPTION STUDY

Batch adsorptions were carried out by shaking 100 ml of fluoride samples in a controlled rotary shaking machine (Model no. CIS-24, Remi Instruments, Mumbai, India) in a glass stopper bottles of 125 ml capacity at different dosages of adsorbent with speed of 150 rpm. The solution was then filtered through Whatman filter paper no. 42 and the filtrate was analyzed for residual fluoride after adsorption in double beam spectrophotometer. All adsorption experiments were conducted at a room temperature and investigate the effect of various parameters like adsorbent dose, pH, temperature, initial fluoride concentrations, contact time etc. The specific amount of fluoride adsorbed was calculated.

RESULTS AND DISCUSSION

Effect of Dose

This experimental study for the estimation of fluoride quantity by using different PPSC doses which evaluated the optimum requirement of dose for the fluoride ions removal from the aqueous solution. The initial fluoride concentration was taken 10.0 mg/L.

The analyzed report shows the % removal efficacy of (PPSC) physically activated charcoal in different doses and quantities. The selected doses such as 0.5 g/L – 5.0 g/L of PPSC were tested and form the experimental analysis it is clearly shows that PPSC is one of the low-cost, effective, bio adsorbent in the process of Defluoridation which shown in fig.6.

The tested results of effect of different doses on the fixed initial fluoride concentration shows as the amount of dose of adsorbent PPSC increases the capacity of % removal of fluoride also increases up to certain extent. The removal % of fluoride increases up to 86.94 for a dose quantity 3.0 g/L. which was

essential to achieve the desired limit of fluoride. The optimized dose 3.0 g/L of PPSC was selected and used for the further study parameters. The fluoride ion removal as it could not follows the drinking water standards given by BIS while the PPSC has a good capacity to remove fluoride ions from aqueous solution.

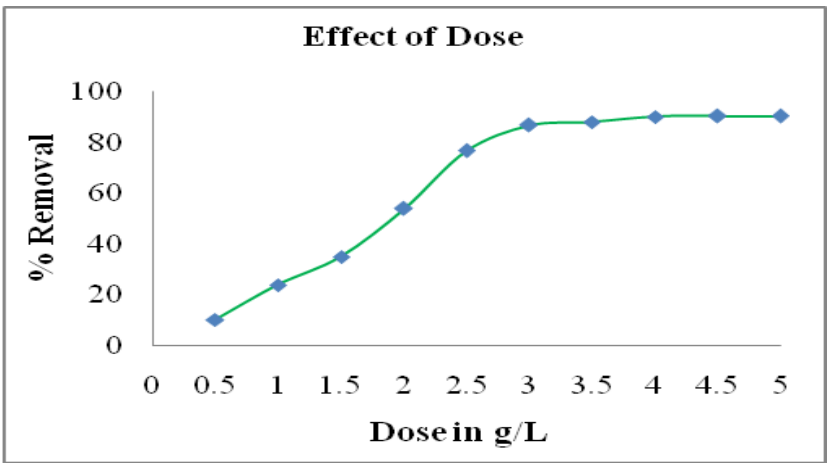

Fig. 6: Dose of Adsorbent Vs. % Removal.
IC: 10 mg/L; pH 7; rpm 150, temp.30^{0}C; Vol. 100 mL

Effect of pH

pH of the synthetic solution of fluoride has a important parameter In the process of removal of fluoride by using adsorption method. This research also proved that the % removal capacity of PPSC is highly depends on the pH of test solution. The pH range consider for this research study was 2-8. The removal efficacy of fluoride was increased with the increase observed up to pH range 6.5 and then after it was observed sudden fall and afterwards removal capacity of fluoride ions decreased with increase in pH as shown in fig.7. The result shows that in lower range the adsorption rate of fluoride ions decreased slightly, it may be due to the formation of weak hydrofluoric acid. The drop of pH recorded due to the competition of the hydroxyl in the process of fluoride adsorption.

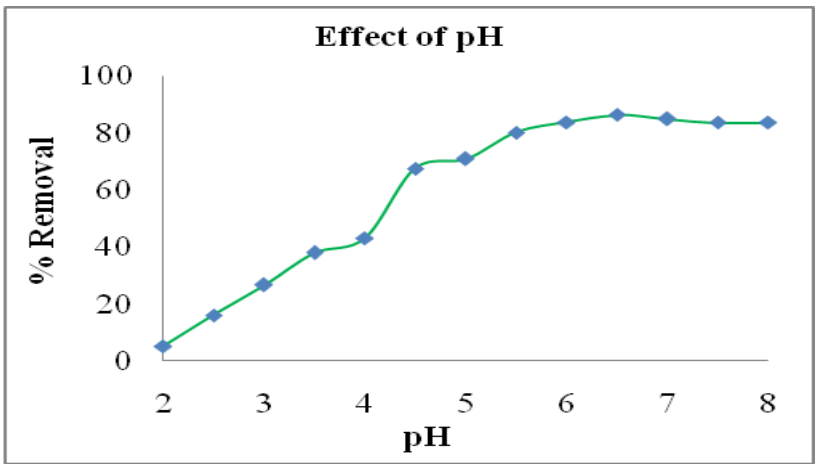

Fig.7: pH Vs. % Removal.
IC: 10 mg/L; pH 7; rpm 150, temp.30^{0}C; Vol. 100 mL

Effect of initial metal ion concentration

In many countries around the world higher fluoride concentrations were observed. In India many states are affected by the higher fluoride concentrations. This parameter of study shows the effect of various initial higher fluoride concentrations and uptake capacity of PPSC in the process of fluoride removal from aqueous solutions. The initial fluoride concentrations 5.0 mg/L to 15 mg/L were studied. The graph stated that the maximum removal capacity in minimum concentration of fluoride available while as the initial concentration of fluoride increases the rate of % removal of fluoride decreases shown in fig.8.

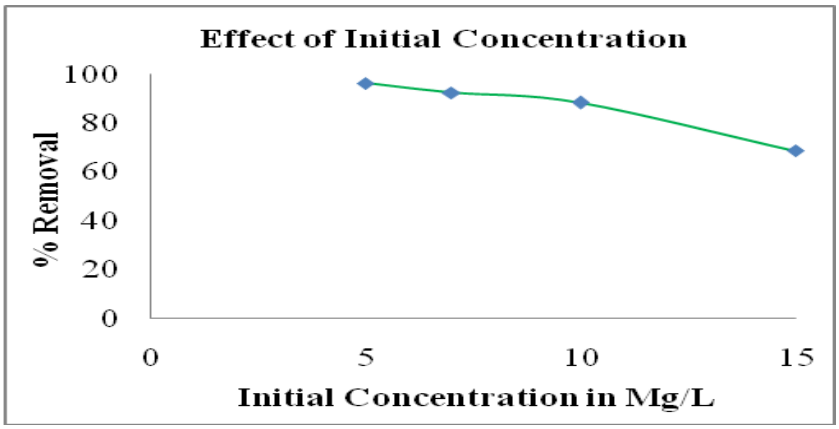

Fig. 8 : Initial Concentration Vs. % Removal.
IC: 10 mg/L; pH 7; rpm 150, temp.30^{0}C; Vol. 100 mL

Effect of Particle Size

Adsorbent particle size has a decisive part in batch adsorption study which affects the process of adsorption. The particle sizes of 75 µm to 300 µm were selected and used in this research. In fig. 9, the result shows that the increase the particle size decreases the removal capacity of fluoride. Hence it proved that the removal capacity of adsorbent is also depends on the particle size of adsorbent used .

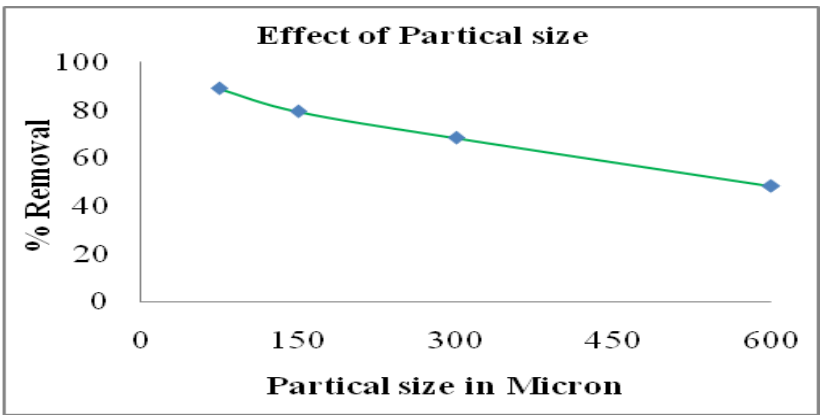

Fig. 9: Particle Size Vs. % Removal
IC: 10 mg/L; pH 7; rpm 150, temp.30^{0}C; Vol. 100 mL

Effect of Contact Time

This study shows the capacity of adsorbent with respect to the time. The analysis shows the PPSC efficiency for different time of contacts. The obtained results show the capacity of PPSC adsorbent increases with increase in contact time. The maximum required fluoride uptake obtained at 480 Min. shown in fig.10.

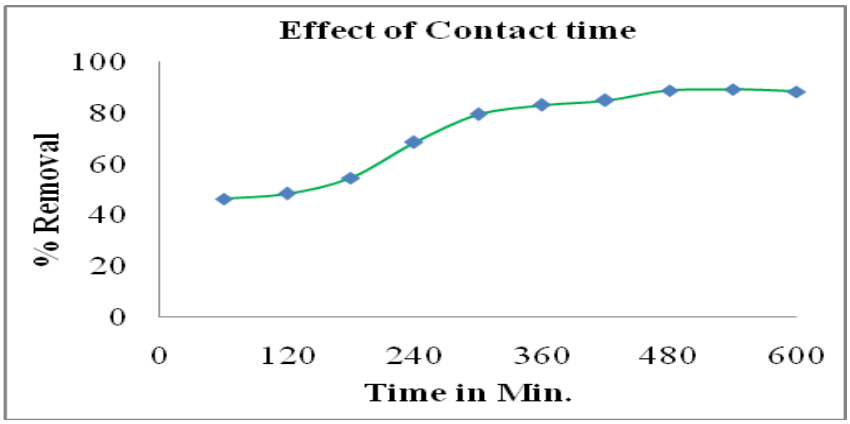

Fig. 10: Contact time Vs. % Removal
IC: 10 mg/L; pH 7; rpm 150, temp.30^{0}C; Vol. 100 mL

ADSORPTION MODEL

Langmuir and Freundlich isotherms were plotted and studied on the basis of analytical data which were well fitted in Langmuir than Freundlich isotherm. This achieved good adsorption capacity of adsorbent.

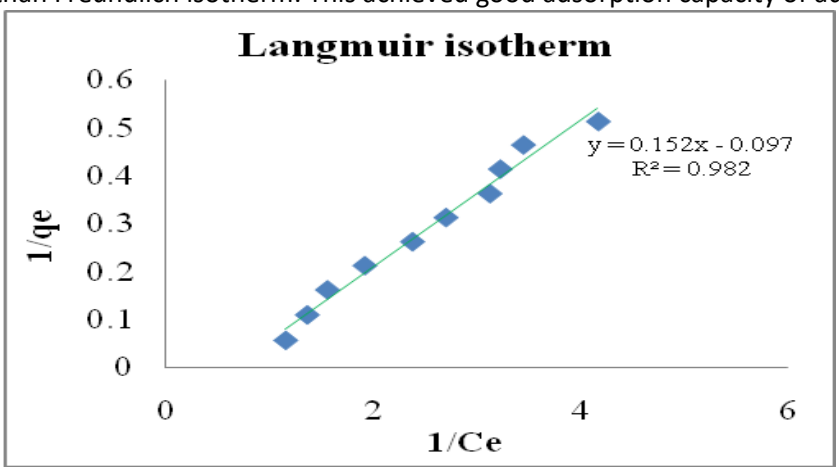

Fig. 11: Langmuir Adsorption Isotherm

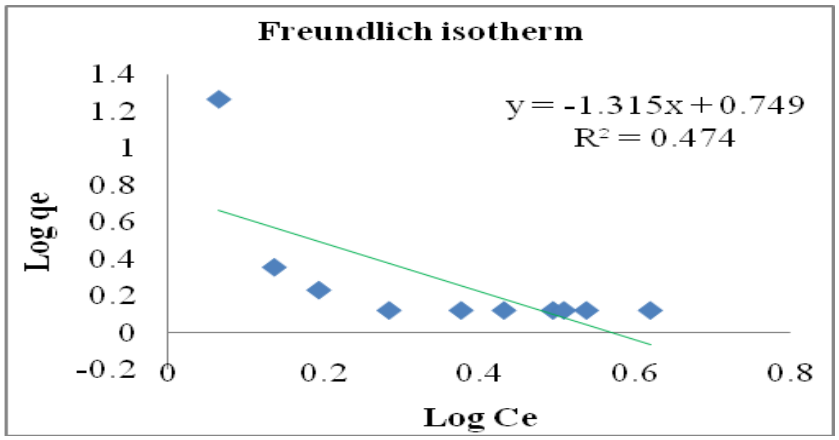

Fig. 12: Freundlich Adsorption Isotherm

In order to attain the good adsorption capacity of the adsorbent, a novel adsorption isotherm was constructed, and the analytical data fitted with Langmuir rather than Freundlich well. The isotherm study's main concern was the interaction between the adsorbent and the adsorbate. The link between the Langmuir and Freundlich adsorption isotherms revealed the information. The Langmuir isotherm is an assumption based on the removal due to monolayer sorption occurring on a homogenous surface of the adsorbent without any collaboration between adsorbed particles, in contrast to the Freundlich isotherm, which is equilibrium based adsorption based on homogeneous surfaces. The equations (a) & (b), which represent the linear equations for the Langmuir and Freundlich isotherms, are given below.

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

Equation (a)

The maximum amount of fluoride that may be absorbed is shown by the term qmax in the equation above, which is expressed in mg/g. The Langmuir isotherm constant, KL, is shown in L/mg, and the equilibrium fluoride concentration, Ce, is shown in mg/L.

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

Equation (b)

In equation 2, Ce is the equilibrium fluoride concentration, qe is the quantity that has been absorbed, and KF is the observational consistency of Freundlich, which is expressed in mg/g. 1/n is the Freundlich type. The Langmuir and Freundlich isotherm application is seen on the direct plot in figures 11 and 12.

CONCLUSIONS

This research study analyzed several parameters and characterizations during the experimentations and on the basis of results found following conclusions are made.

- ❖ PPSC is a predominant adsorbent found in the process of Defluoridation.
- ❖ PPSC required pre-treatment of physical activation before the used as an adsorbent.
- ❖ Optimum dose of PPSC was found 3.0 g/L for the removal of fluoride concentrations 10 mg/L.
- ❖ Adsorption capacity found more up to pH 6.5 and then it was falls down.
- ❖ Optimum time of contact was found 480 Min.
- ❖ Adsorption capacity of PPSC was found more on particle size of 75 micron at standard conditions.
- ❖ In adsorption Freundlich and Langmuir models were tested and found the best fitted model was Langmuir than the Freundlich.
- ❖ All the physicochemical parameter of drinking water was found within permissible limits (BIS 10500 - 1991) after treatment.

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