Reduction of Fluoride in Drinking Water using Azadirachta Indica (Neem Leaves)

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Abstract—Fluoride is a persistent and non–biodegradable pollutant that accumulates in soil, plants, wildlife and in a human being. Therefore, removal of fluoride, using best technique with optimum efficiency is needed. The present survey highlights on efficiency of different materials for the removal of fluoride from water. The study assess the suitability of inexpensive leaf adsorbents to effectively remediate fluoride contaminated water. In present study neem leaves powder activated using chemical treatment as a low cost adsorbent and its characteristics were studied. The most important results of extensive studies on various key factors (pH, contact time, temperature, particle size, surface area, adsorbent dosage) fluctuate fluoride removal capacity of materials are reviewed. The adsorption equilibrium is well correlated by freundlich and Langmuir models. Langmuir isotherm fits well for defluoridation of water using leaf powder. The percentage of fluoride removal using the low cost adsorbents are as follows, inactivated adsorbent – 91% activated adsorbent = 85%, carbonized adsorbent = 87%.

Key words: Fluoride Ion, Low Cost Adsorbent, Adsorption, Langmuir Isotherm

I. INTRODUCTION

Fluoride is the ionic form of fluorine. Fluoride is often used in pesticides, dentistry and is added to the municipal water supplies in the community. The chemical nature of water is one of the most imperative criteria that determine its usefulness for a precise need and as such not all the waters are fit for drinking and potable purposes. Apart from fluoride, arsenic and nitrate are few of major water pollutants.

According to the World Health Organization the maximum acceptable concentration of fluoride ions in drinking water lies below 1.5 ppm. Fluoride if taken in small amount is usually beneficial, but the beneficial fluoride concentration range for human health is very small. Depending on the concentrations and the duration of fluoride intake, it could have positive effect on dental caries.

On the contrary, long term consumption of water containing excessive amounts of fluoride can lead to fluorosis of the teeth and bones. This review paper focuses on removal of excess fluoride in drinking water by using low cost adsorbent (Neem). In this review adsorption technique is widely used. Adsorption is one of the established unit operations used for the treatment of contaminated water i.e., raw water and/or wastewater.

In Tamil Nadu, the high concentration of fluoride in groundwater is found to be in Dharmapuri and Salem district closely followed by Coimbatore, Madurai, Trichy, Dindukul and Chidambaram district. The districts having low fluoride are Thirunelveli, Pudukottai, North Arcot, and Ramanad districts. The district wise fluoride status in Tamil Nadu is presented in Table 1.4. Fluoride in Tamilnadu

II. REVIEW OF LITERATURE

Alagappan Sethuraman et.al presents of high concentration of fluoride in drinking water causes dental and skeletal fluorosis in humans in several parts of the world. In India presence of high concentration of fluoride in water is reported from different corners of the country. In the present study we investigated fluoride levels in the Uppanar estuary water in Cuddalore, Tamil Nadu, India. Forty five water samples from different villages located near SIPCOT Industrial Zone, Cuddalore, were collected and analysed for fluoride concentration. Water samples were collected during May to June in 2008. It was recorded that in the water of Thaikkal village fluoride concentration were ranged between 1.8 and 2.4 mg/l, and in Kudikadu values of fluoride concentration were between 01.1and 2.1 mg/l. Moreover, the fluoride concentration in water near the SIPCOT Zone ranged between 1.0 and 1.7 mg/l. The concentration of fluoride (2.4mg/l) recorded from these sites were higher than the WHO recommended safe levels of fluoride in drinking water resources. Since the fluoride concentration recorded in the present study are above 1 mg/l, it may lead to skeletal fluorosis which has no treatment or cure at present and hence appropriate steps have to be taken to prevent such fluorosis in these villages. Sutapa Chakrabarty et.al Discuss the Drinking water quality with respect to fluoride, iron, and nitrate content has been carried out in Kamrup district of Assam, India. Forty six different sampling stations were selected for the study. Iron was analyzed by using an atomic absorption spectrometer, Perkin Elmer AA 200, while fluoride was measured by the SPADNS method at 570nm and Nitrate content was measured by the phenol-disulphonic acid method at 410nm using a UV–VIS spectrometer, Shimadzu 1240 model. The study revealed that the water sources in the area are heavily polluted with iron, and fluoride. Statistical analysis of the data is presented to determine the distribution pattern, localization of data and other related information. Statistical observations imply nonuniform distribution of the studied parameters with a long asymmetric tail either on the right or left side of the median. Ghanshyam Pandhare et.al presents the adsorption technique is effective and economical to application level. The regular commercial activated carbon is expensive, so there is a need of alternatives for such application. In present study Neem leaves powder activated carbon has developed as an adsorbent. In the textile industry, the activities involving dyeing generate pollutants due to the discharge of toxic effluents, originating from the byproducts generated. If not treated properly before being discharged into natural water bodies, the effluent from this
industry may reach potable water resources, causing serious ecological concern. Therefore the development of new technologies for the removal of color from waste water is necessary. The aim of this work is to study the color removal by Neem Leaves Powder from methyl red & K2Cr2O7 solution and to offer this biosorbent as local replacement for existing commercial adsorbent materials.

A. Sample collection
The neem leaves were collected from the P.S.R Engineering College, Sivakasi. They were washed with water to remove dust and other impurities. It is used as a absorbing media. These plants are easily available in the region.

B. Preparation of activated adsorbent
The neem leaves are burnt in the thermal furnace at 300˚C for 3 hours. The neem leaves were ground to obtain small pieces. They were mixed with H2PO4 (1:2) to increase the porosity at a range of 500˚C for 3 hours. The dried material were ground and sieved through standard sieves. Thus the activated carbon is prepared.

C. Batch study
Batch adsorption tests were conducted to investigate the effect of controlling parameters like pH, adsorbent dosage, size of adsorbent and contact time. All the experiments were conducted at room temperature. All optimization experiments were performed with the synthetic sample of 4ppm fluoride. The experiment was used to study the effect of adsorbent dose which was carried out at 15 minutes contact time, pH, and ambient temperature. The effect of contact time was studied at dose of adsorbent were taken as 0.4g/50ml.

After desired contact period, conical flasks were removed and allowed for two minutes to settle down the biosorbents. The solutions were filtered through the filter papers. The filtrate was then analyzed according to the SPANDS method as prescribed in standard methods of water and waste water analysis (APHA, 2005).

In both process studies pH, adsorbent dose, contact time was optimized on the synthetic sample of 4ppm of fluoride was also studied.

D. Adsorbate preparation
1) Preparation of Stock Fluoride Solution:
The fluoride solution is prepared by dissolving 221mg of a hydrous sodium fluoride (NaF) in distilled water and then diluted to 1 lit.

2) Preparation of Fluoride Standards:
The standard solutions of fluorides are prepared by taking 10 ml of stock solution and diluted to 100 ml. A series of standard fluoride solutions are prepared in the range of 0.0 to 5.0 mg/lit at intervals of 0.5 mg/lit, by dilution of stock solution with distilled water.

3) Spands Solution Preparation:
958 mg SPANDS is dissolved in the distilled water and diluted to 500 ml. This solution is stable indefinitely if protected from sunlight.

E. Zirconyl acid reagent
133 mg of zirconyl chloride is dissolved in about 25 ml of distilled water and add 350 ml of concentrated HCl and dilute to 500 ml with distilled water.

F. Mix solution
Equal volume of SPANDS solution and zirconyl acid reagent is mixed for getting the mix solution. The combined reagent is stable for at least 2 years.

G. Reference solution
10 ml of SPANDS solution is added with 100 ml distilled water and 7 ml of concentrated HCl is diluted to 10 ml and then it is mixed with the diluted SPANDS solution. The resulting solution, used for setting the reference point (Zero) of the spectrometer. This solution is very stable and may be reused indefinitely.

H. Isotherm study
Defluoridation capacity was evaluated using the Langmuir and Freundlich adsorption isotherms.

I. Langmuir isotherm study
Langmuir equation which is valid for mono layer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface.

\[
\frac{C}{q_e} = \frac{1}{Q_o h} + \frac{C_e}{Q_o}
\]

Where,

- \( C_e \) = Concentration of fluoride in aqueous phase at equilibrium (mg/l)
- \( Q_o \) = Maximum capacity of adsorbent (mg/g)
- \( h \) = Langmuir constant

J. Freundlich isotherm study
The Freundlich isotherm in its linear form is represented by

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln C_e
\]

Where,

- \( q_e \) = Amount of fluoride (mg/g) at equilibrium at time \( t \)
- \( C_e \) = Initial concentration of fluoride (mg/l)
- \( C_i \) = Initial concentration of fluoride at equilibrium (mg/l)
- \( M \) = Amount of biosorvents used (g)

K. Kinetics study
To understand the kinetics of the process, the data was fitted to different rate equations. A general rate expression takes the form \( dq/dt = K n (q_e - q_t) \) with \( n \) being the rate of the process.

L. Pseudo - first order kinetics study
A pseudo-first-order rate expression, or the Lagergren rate equation, is expressed as

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

where,

- \( q_e \) and \( q_t \) are the amount of fluoride (mg/g) at equilibrium at time \( t \), respectively,
- \( K_1 \) is the first-order rate constant.

M. Pseudo-Second Order Kinetic Model
A pseudo-second-order expression may be derived as

\[
t/q_t = (1/K_2) (1/q_e^2) + t/q_e
\]
Where, 
q_e and q_t are the amount of fluoride (mg/g) at equilibrium at time t, respectively, and 
K_2 is the second-order rate constant.

N. Comparative Study
Comparative study is done with the inactivated, activated and carbonized adsorbent. In this comparative study inactivated adsorbent is found to be more effective and hence inactivated adsorbent can be used for further removal of fluoride.

III. RESULTS AND DISCUSSIONS
A. Adsorption Studies
Successful application of the adsorption technique demands innovation of cheap, nontoxic,easily and locally available material. Bioadsorbents meet these requirements. Knowledge of the optimal conditions would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact, time, and amount and particle size of adsorbent and concentration of fluoride ions of the uptake on adsorbent materials was investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the rate and equilibrium data.

B. Photometer Reading and Percentage of Adsorption
The collected solution after the experiment is used for calculating percentage adsorption. At first the reading for water is taken which is the blank reading. Then photometer reading taken for all sample solution. This is reference reading. Reduce concentration of solution calculate from graph of SPANDS solution photometer reading. The percentage adsorption of all sample calculated by following formula,
\[
\% \text{ Adsorption} = \left( \frac{\text{Initial conc.} - \text{Final conc.}}{\text{Initial conc.}} \right) \times 100
\]

C. Influence of Adsorbent Dosage
The removal of fluoride ions increases with an increase in amount of adsorbent. The amount of adsorbent dose was varied between 0.5 g. Results showed maximum removal of 91% was observed at 0.4g at room temperature.

Following tables shows the absorbance reading and absorbance concentration in fluoride solution using various times of adsorbent.

Based on the analysis it is obtained that the percentage of removal of fluoride ion increases with increase in doses from 0.1g to 0.6g. There was a non-significant increase in removal of percentage of fluoride when adsorbent dose increases beyond 0.3g i.e. accurately about 0.4g. This suggests that after a certain dose of bio adsorbent the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of dose adsorbent. The increase in fluoride removal percentage with increase in adsorbent dose is due to the greater availability of the surface area at higher dose of the adsorbent.

D. Influence of Adsorbent Particle Size
Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of fluoride ions. Particle size analysis was conducted on treated biosorbents and the percentage composition of particle size was investigated. The presents of large number of smaller particles provide the adsorption system with the large surface area available for fluoride ion removal. The removal of fluoride ion has been studied at a room temperature.

Based on the studies it is evaluated that the influence of adsorbent particle size for a constant weight on the removal of fluoride ions. With the largest particle size of 300 microns the amount of fluoride ions adsorbed was found to be 50% treated biosorbents and about 90 to 95% with the smallest particle size of 75 micron for an initial fluoride ion concentration of 0.4 mg/l respectively. This study gives some idea of rate limiting step of the adsorption process.

E. Influence of Concentration
For a strictly adsorptive reaction in the optimized period of contact the rate various directly with the concentration of adsorbate. The capacity of adsorbent material gets exhausted sharply with increase in initial fluoride ion concentration. The adsorption capacity of treated biosorbents was systematically studied by varying the initial concentration of fluoride ions. It is found that the percentage removal of fluoride ion increases with increase in concentration from 2ppm to 6ppm. There was a non-significant increase in removal of percentage of fluoride when adsorbent concentration increases beyond 3ppm i.e. accurately about 4ppm. This suggests that after a certain concentration of bio adsorbent the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of concentration adsorbent. The increase in fluoride removal percentage with increase in adsorbent concentration due to the greater availability of the surface area at higher concentration of the adsorbent.

F. Effect of pH
The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was examined at pH values of 2, 4, 6, 8, and 10. This was adjusted by adding 0.5N HNO3 or 0.1M NaOH with 50 ml of standard solution of 10 mg/l of fluoride for a contact time of 15 min with a dose of 10 g/l of treated biosorbent. We have observed decrease in the extent of removal of fluoride ions with increasing in the pH of the solution. This was investigated as 80% at pH 6 and 70% in the case of treated biosorbents. Hence further studies were conducted within these pH values. In the case of treated biosorbents, the percentage of adsorption increased almost linearly between 6.0 and 9.0, retaining a maximum removal at pH 7.0 in 15 min of contact time. In this case, the result may be due to neutralization of the negative charges at the surface of the treated biosorbents by greater hydrogen ion concentration at lower pH values. This reduces hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of treated biosorbents.

G. Isotherm Study
The adsorption data for the removal fluoride ion correlated with Langmuir and Freundlich methods.
H. Langmuir Isotherm Study

Langmuir isotherm is based on the assumption that point of valence exits on the surface of the adsorbent and that each of these sites is capable of absorbing one molecule. Thus, the adsorbed layer will be one molecule thick. The Langmuir equation is commonly written as

\[
\left( \frac{C_e}{q_e} \right) = \left( \frac{1}{hQ_o} \right) + \left( \frac{C_e}{Q_o} \right)
\]

Where,

- \( C_e \): Concentration of fluoride in aqueous phase at equilibrium (mg/l)
- \( Q_o \): Maximum capacity of adsorbent (mg/g)
- \( h \): Langmuir constant.

When \( C_e \) is plotted against \( C_e / q_e \), a straight line with slope is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Fig. 1.

Fig. 1: Linear model of Langmuir isotherm

J. Kinetic Study

Based on the kinetics studies it is analyzed that PSEUDO SECOND ORDER is suitable for the fluoride removal.

K. Comparative Study

Comparative study is done with the inactivated, activated and carbonized adsorbent. In this comparative study inactivated adsorbent is found to be more effective and hence inactivated adsorbent can be used for further removal of fluoride.

Inactivated adsorbent = 91%
Activated adsorbent = 87%
Carbonized adsorbent = 80%

IV. CONCLUSION

In present work attempt have been made for systematic studies of removal of fluoride using low cost adsorbent prepared from neem leaves. From this experimental finding...
it has been observed up to 90% for prepared neem leaves as optimum value of parameter. Adsorption equilibrium was achieved within 15 minutes. The process of adsorption by treated adsorbent follows Langmuir isotherm, which comprises statistical and empirical data estimated from isotherm equation. Although regression coefficient of both pseudo first and second order lot indicates adherence of both the rate laws but higher regression value of first order plot than the second order plot reaction indicates the adsorption follows the second order rate laws. It was seen that the amount of sample is increased the percentage of adsorption also increases. Thus from the studies carried out it can be conclude that the prepared inactivated carbon can be used effectively to adsorb fluoride. There’s a tremendous potential in these materials to be explored as industrial low cost effective adsorb.

REFERENCES