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Defluoridation of water using Mentha longifolia (Mint) as Bioadsorbent

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ABSTRACT
Excessive fluoride concentrations have been reported in ground waters of 19 states of India. Acute fluorosis is noticed in many problem areas of these states. In spite of several existing physical and chemical defluoridation methods, there is an urgent need to develop cost effective and biodegradable methods to effectively treat high fluoride concentration in ground water. Experiments at room temperature were performed to evaluate the adsorption capacity of Mentha longifolia (Mint) from aqueous solutions. 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 is investigated from kinetic viewpoint. Adsorption studies are performed by batch technique to obtain the rate and equilibrium data. The Freundlich and Langmuir sorption isotherms were used to quantify sorption properties. Results show that Mentha longifolia (Mint) is effective in removing fluoride from groundwater samples.

Key words: Defluoridation; Biosorption; Mentha longifolia; pH; Adsorption kinetics.

INTRODUCTION

Free fluorine plays no part in toxicology because it reacts immediately to form fluoride compounds. The presence of dissolved fluorides in natural waters is possible only when favorable conditions facilitate long residence times of the F- species in solution. Occurrence of fluorine in groundwater has drawn worldwide attention due to its considerable impact on human physiology. The permissible limit of F^- in drinking water is 1.5 mg/l (W.H.O 1984). It is generally accepted that fluoride stimulates bone formation (Richards et al., 1994) and optimum concentration of fluorides have beneficial effects on the teeth by hardening the enamel and reducing the incidence of dental caries (Fung et al., 1999). At lower levels (<2 ppm) soluble fluoride in the drinking water may cause mottled enamel during the formation of teeth, but at higher levels other toxic effects may be observed. Excessive intake of fluoride results in skeletal and dental fluorosis (Czarnowski et al., 1999). Fluorides in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested. Fluoride is beneficial especially to young children below eight years of age when present within permissible limits of 1.0-1.5 mg/L for calcification of dental enamel. Excess fluorides in drinking water cause dental fluorosis and/or skeletal fluorosis (Sorg, 1978). The main source of fluoride in the groundwater is fluoride bearing rocks. Such host rocks due to weathering leach out fluoride and contaminate the ground water. Fluorides occur in three forms, namely fluorspar or calcium fluoride (CaF2), apatite or rock phosphate (Ca_3F $(PO4)_3$) and cryolite (Na_3AlF_6) (Sunitha et al., 2012). Defluoridation means the removal of excess fluoride from water (Jamode et al., 2004; Saha S, 1993).The National Environment Engineering Research Institute (NEERI), Nagpur, India has evolved an economical and simple method of defluoridation, which is referred to as the Nalgonda technique. UNICEF has worked closely with the Government and other partners in defluoridation programmes in India, in the areas of excessive fluoride in groundwater. In the 1980s, UNICEF supported the Government's Technology Mission to identify and address the fluoride problem and the Government subsequently launched a massive programme, still under way, to provide fluoride-safe water in all the areas affected (Ranjeeta, 2015). Defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available. After the discovery of fluoride as the cause of fluorosis, extensive research has been done on various methods for removal of fluoride from water and wastewater. These methods are based on the principle of adsorption (Raichur et al., 2001) ion-exchange (Singh et al., 1999), precipitation–coagulation (Saha et al., 1993; Reardon, 2000), membrane separation process (Amer et al., 2001; Dieye et al., 1998), electrolytic defluoridation (Mameri et al., 2001) and electro dialysis (Hichour et al., 1999; Hichour et al., 2000; Adhikari et al., 1989) .

The various adsorbents that have been used for fluoride removal are alumina, alumina in combination with manganese dioxide, iron oxide, calcium minerals. Also, several clays and soils have been tried as an adsorbent medium for defluoridation. A technology for the granulation of Fe-Al-Ce nano-adsorbent (Fe-Al-Ce) in a fluidized bed has also been developed

(Lin Chen et al., 2009). Defluoridation studies based on membrane techniques and the use of reverse osmosis (RO) membranes for fluoride removal from contaminated water sources were reported earlier. However, this technique has not been successful due to low permeate fluxes. Moreover, the process also generates more concentrated waste as reject (Anand Babu et al., 2011). In addition, due to high cost or lower efficiency or non-applicability on mass scale, these techniques are not in use. This paper presents the findings of an investigation on the use of leaf powder of Mint leaves (Pudina) for the defluoridation of water.

MATERIALS AND METHODS

All the reagents used were of AR grade. Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 mL distilled water and using this stock solution, fluoride standard solution is prepared by diluting 100 mL stock solution to 1000 mL distilled water in volumetric flask. This 1 mL solution has 0.1 mg of fluoride. The biomass powder is treated with acid and alkali treatment. Fluoride ion is determined by Orion ion meter as per standard methods. pH meter, and shaking machine for agitating the samples for the required period at a speed of 200 strokes/minute are used. The surface area of the adsorbent particle, porosity and density are measured by using surface area analyzer, mercury porosimeter and specific gravity bottles, respectively.

The most important electro analytic method for determination of fluoride ion in water solution is usage of ion selective electrode for fluorides. Fluoride selective electrode is very sensitive, and temperature range of electrode varies from 0 to 50°C. For potentiometric analysis of fluoride ion, electrodes with homogenic membrane made from fluoride lantana (LaF3), which was first suggested by Frant and Ross are mostly used commercially (Frant and Ross, 1966; Frant, 1994; Frant, 1999).

The great selectivity of electrode is important as only fluoride ions are included in the process of diffusion (Cammann, 1979).The potentiometric method is based upon measurements of the potential electromotive force of a galvanic element. Direct potentiometric determinations are almost always performed using ion selective electrodes (ISEs), which are capable of rapid and selective measurements of analyte concentration (Sunitha et al., 2014).

Material Development

Fresh leaves chosen from mint plant (Pudina) are sun-dried for 3-4 days, put in a cotton jute bag and crushed manually (This process can save the energy expended in hot air oven drying and mechanical crushing). The powder was sieved to get various particle sizes, viz. 600 m, 710 m, and 850 m, 1 mm, and 1.4 mm. Leaf powder biomass was further digested by chemical methods.

Sorption Studies

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 is investigated from kinetic viewpoint. Adsorption studies are performed by batch technique to obtain the rate and equilibrium data. Experiments are carried out by shaking 10 g/L of adsorbent dose with 50 mL of aqueous solution containing known concentration of fluoride ions and by agitating the samples on shaking machine at a speed of 200 strokes/min. Samples containing fluoride ions are maintained at a desired pH (5-6) by adding 0.5N HNO_3/0.1M Na OH. All the experiments are conducted at room temperature (29 ± 0.5°C). Preliminary investigations on the uptake of fluoride ions on the adsorbent material at their optimum pH values indicate that the processes are quite rapid. Typically, 80% of the adsorption occurs within the first hour of the contact for fluoride ions with an initial concentration and adsorbent dose of 10 mg/L for treated bio-sorbents.

Sorption Mechanism

The sorption data for the removal of fluoride ions has been correlated with Freundlich and Langmuir models (Jamode et al., 2004).

I. Freundlich Equation:
It has the general form of

$$q_e = K_f C^{1/n}$$

The linearised Freundlich adsorption isotherm, which is of the form

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

where q_e is the amount of metal ions adsorbed per unit weight of adsorbents (mg/g), K_f and 1/n are the Freundlich constants, if $1/n < 1$, bond energies with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$ all surface sites are equivalent. C_e is the equilibrium concentration (mg/L). Linear plots of log q_e(x/m) vs log C_e at different adsorbent doses are applied to confirm the applicability of Freundlich models as shown in Figure.1. The calculations for Freundlich model for the removal of fluoride ions are shown in Table 1.

II. Langmuir isotherm
Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is fit for adsorbing one molecule. Thus, the absorbed layer will be one molecule thick. Moreover, it is expected that all the adsorption destinations have break

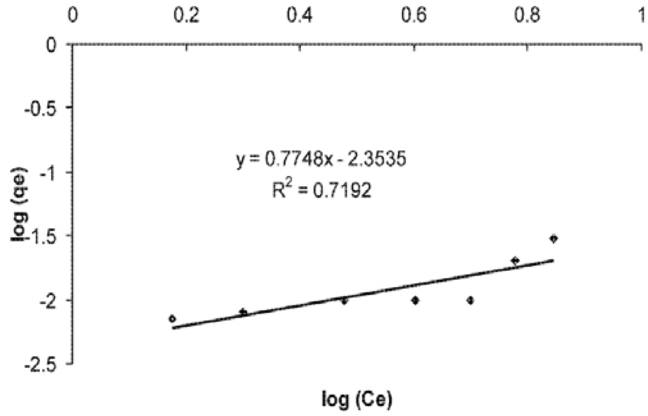

Figure 1. Linear model of Freundlich isotherm**.**

Table 1. Calculation of Freundlich isotherm.

Dose (mg/L)	C_e (mg/L)	Q_e (mg/g)	$1/C_e$	$1/q_e$
50	8	0.04	0.9031	1.4
100	7	0.03	0.8451	-1.6
200	6	0.02	0.7782	-1.7
500	5	0.01	0.699	-2
600	4	0.01	0.6021	-2
700	3	0.01	0.4771	-2
1000	2	0.008	0.301	-2.097
1200	1.5	0.0071	0.1761	-2.15

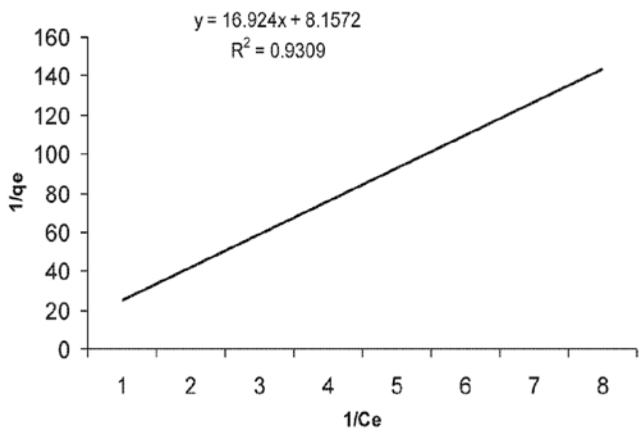

Figure 2. Linear model of Langmuir isotherm.

even with affinities for particles of the adsorbate and that the vicinity of adsorbed atoms at one site won't influence the adsorption of atoms at a nearby site. The Langmuir mathematical statement is normally composed as

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

where q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L), Q_o and b are the Langmuir constants related to capacity and energy of adsorption, respectively.

The linear form of the Langmuir isotherm can be expressed as,

$$1/q_e = (1/Q_o) + (1/bQ_oC_e)$$

Whenever $1/q_e$ is plotted against $1/C_e$, a straight line with incline $1/bQ_o$ is obtained. This demonstrates that the adsorption takes after the Langmuir isotherm, as shown in Figure 2. The Langmuir constants b and Q_o are figured from the slant and catch with Y-pivot. The key attributes of a Langmuir isotherm can be communicated as far as

Table 2: Calculation of Langmuir isotherm.

Dose (mg/L)	C_e (mg/L)	Q_e (mg/g)	$1/C_e$	$1/q_e$
50	8	0.04	0.125	25
100	7	0.03	0.1429	33.3
200	6	0.02	0.1667	50
500	5	0.01	0.2	100
600	4	0.01	0.25	100
700	3	0.01	0.3333	100
1000	2	0.008	0.5	125
1200	1.5	0.0071	0.6667	141

dimensionless detachment consider and depict the sort of isotherm characterized by,

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

where b and C_o are terms appearing in Langmuir isotherm.

From figures 1 and 2, it is found that the R^2 value for Langmuir model is near to unity and hence the process of defluoridation using treated biosorbent follows well the Langmuir isotherm. Table 2 gives the calculations of Langmuir model for the removal of fluoride ions and the various constants of this model.

CONCLUSION

Results demonstrate that these minimal effort bioadsorbents could be productively utilized for the evacuation of fluoride over an extensive variety of fixations. Treated biosorbents are seen to be effective for the uptake of fluoride particles somewhere around 2.0 and 10.0 pH. Fluoride removal for a given bio-adsorbent size increased with time attaining equilibrium within 1.5 h. The rate of fluoride removal is observed to be a component of adsorbent dosage and time at a given introductory solute concentration. It expands with time and adsorbent dosage; however, higher initial solute fixation will diminish the time and adsorbent dosage. Biosorbents absorption method follows the Langmuir isotherm, which comprises statistical and empirical data estimated from Isotherm equation. The adsorption capacity of treated biosorbents is studied by varying the initial concentration of fluoride ions between 2 and 15 mg/L. With the largest particle size of 1.4 mm, the amount of fluoride ions adsorbed is found to be 95%. With smallest particle size of 600 μ for an initial fluoride ion concentration of 10 mg/L, 90% adsorption is observed. Small particle size provides more active surface area and hence such results. Treated biosorbents can be removed effortlessly. There is no compelling reason to recover the depleted biosorbents as they are accessible bounteously, effortlessly, economically and locally. This system is financially perceptive, environment friendly and straightforward and can be embraced in provincial and also urban foundation consistently. Water filtration systems are frequently costly or inadmissible for the situations where they are generally required. The developed technique reported in this study has the advantages of high fluoride removal capacity, ease of operation, economic, environmental friendly and thus making this approach is most desirable to the people, especially in the rural areas with high ground water flouride contaminations.

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Compliance with Ethical Standards

The authors declare that they have no conflict of interest and adhere to copyright norms.

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Quotations on Fluoridation and de-fluoridation of water

“There is significant evidence to suggest that the risks from the use of fluoride for prevention of tooth decay exceed any questionable benefit that is achieved.

Clarence Brown (1890 -1987) was an American film director.

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“The health risks associated with the use of fluoride in drinking water outweigh, to a significant degree, the slight benefits from that use.”

Phillip M. Allen (1939 -2012) was an American stage, film, and television actor.

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Fluoride seems to fit in with lead, mercury and other poisons that cause chemical brain drain. The effect of each toxicant may seem small, but the combined damage on a population scale may be serious, especially because the brain power of the next generation is crucial to all of us.”

Philippe Grandjean (1950--) is a Danish scientist working in environmental medicine.