FLUORIDE REMOVAL FROM DRINKING WATER BY PRISTINE PUMICE AS ADSORBENT

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ABSTRACT

Higher levels of Fluoride concentration in drinking water is a matter of serious concern in the present scenario. Controlling the Fluoride levels within the permissible range is of utmost importance to Human beings. The potential of pristine pumice to be used as an adsorbent for the elimination of fluoride from the drinking water is examined. The experiments are performed in batch equilibrium techniques. The influence of varying sorbent concentration, contact time and initial concentration of fluoride was also studied. It has been observed that the fluoride removal is directly proportional to the contact time and sorbent dose. The increase in the reaction period and the sorbent dose improved the quantity of fluoride adsorbed. The present study has indicated that an increase in fluoride initially present results in low efficacy of percentage removal. The adsorption process was found to follow the Langmuir Isotherm.

Keywords: Pumice, Adsorption, Fluoride Removal, Batch Techniques

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INTRODUCTION

Water is an indispensable resource for both biotic as well as abiotic components. About 70% of Earth's surface is covered with water resources out of which 96% falls under Oceans and Seas and is rendered unfit for drinking due to the high salinity. Ice caps, glaciers, and permanent snow constitute approximately 1.7% of the total water. Only a small portion of water is available as groundwater which can be accessed by human beings. In India, 67% of the total population resides in the rural area and groundwater forms the basic source for satisfying their drinking as well as agricultural needs¹. But nowadays it has become problematic as the water has become severely contaminated due to natural and anthropogenic factors. Water consists of numerous ions like SO_4^{2-} , Mg^{2+} , Ca^{2+} , F^- etc. Out of this, Fluoride tends to have both a positive as well as a detrimental effect on human health. The prevalence of fluoride in water aids the formation of enamel and bones in children and animals. Fluoride content up to 1mg/litre is considered beneficial for humans as prescribed by the Bureau of Indian Standards (BIS)². World Health Organisation (WHO) has laid down a limitation on the concentration of fluoride at 1.5mg/litre in potable water³. Consumption of water with fluoride content greater than the permissible limit results in the development of white patches which further leads to dental fluorosis characterized by brown staining followed by pitting of teeth. The prolonged consumption of contaminated water with fluoride concentration exceeding 8 mg/litre results in pain in the joints and brittleness of bones. The intake of fluorides more than 20 mg/day over 20 years or more might result in chronic fluorosis⁴. Dental and skeletal fluorosis are encountered due to the affinity of positively charged calcium ions in bones and teeth to the highly electronegative fluoride ions. Nausea, alterations in the functioning of the kidney, digestive system, central nervous system, nervousness, mottling of teeth, dwarfism, reduced immunity are the other problems associated with the intake of fluoride-rich water. The severity of the problem depends on various factors like contact time of water with the aquifers, pH, climatic conditions, solubility of fluoride minerals, evaporation rate.

Out of all the elements in the periodic table, Fluorine is known for its highest electronegativity and reactivity. It is the thirteenth most abundant element in the earth's crust. On the virtue of its high reactivity, it does not occur in its natural state in groundwater. The minerals containing fluoride are Apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{Cl}, \text{F}, \text{OH})$], Topaz [$\text{Al}_2\text{F}_2(\text{SiO}_4)$], Cryolite (Na_3AlF_6), Fluorspar (CaF_2), Villiumite (NaF). These minerals are found to be almost insoluble in water. Therefore, the traces of these minerals will be present in groundwater only when the conditions are favourable⁶.

Table-1: Effect of Fluoride on Public Health⁵

Fluoride (F) Concentration (mg/litre)	Health Effect
< 0.5	Dental carries
0.5 - 1.5	Optimum Dental Health
1.5 - 4.0	Dental fluorosis
4.0 - 10	Dental and Skeletal fluorosis
>10	Crippling fluorosis

The occurrence of fluoride is mainly on the account of seepage of rainwater through the ground surface. The presence of fluoride is primarily on the account of the weathering of fluoride-rich rocks due to the rock-water interaction which often depends on the velocity of water, residence time and the solubility of fluoride minerals in the water. Consequently, fluoride from the rocks is leached out and augments the fluoride content in groundwater. Seawater has a fluoride concentration of roughly 1mg/litre. Groundwater quality in many areas is adversely affected by the fluoride and is presently 67mg/litre whereas surface water has a fluoride concentration of less than 0.1mg/litre. Foodstuff like fish and tea also contains fluoride to some extent. Although foodstuffs contain trace quantities of fluoride, it is the drinking water that accounts for 60% of the total intake of fluoride and makes fluorosis pandemic⁷. The other sources contributing to the deleterious effects of fluoride are toothpaste, phosphate fertilizers, volcanic activity, etc.

Globally, it was estimated that 260 million people were exposed to water consisting of fluoride greater than 1 mg/litre and the greatest problem was reported in China, India, Sri Lanka and few parts of Africa⁸. In India, Andhra Pradesh was the first state to face the issue of excessive fluoride in potable water in the year 1937⁹. Approximately 65% of India's villages and 62 million people are suffering from fluorosis¹⁰. The contamination was adverse in Andhra Pradesh (1.8-8.4 mg/litre), Haryana (1.5-17 mg/litre), Punjab (0.44-6 mg/litre), Rajasthan (1.54-11.3 mg/litre), Gujarat (1.6-6.8 mg/litre), Tamil Nadu (1.5-3.8 mg/litre) and Uttar Pradesh (1.5-3.11 mg/litre) as per the groundwater testing carried out in the districts in 2201¹¹.

Due to the deterioration of water quality and subsequent health implications, it is crucial to get rid of fluoride from drinking water before its utilization. For this purpose, various techniques have been adopted like the Nalgonda technique, Adsorption, Electrocoagulation, Membrane Filtration, etc. Adsorption is also known to be effective in the removal of heavy metals. For example, Nano adsorbents aid in the extraction of heavy metals from water¹². A study reported satisfactory results on the removal of heavy metals and dyes using Nano adsorbents and plant residue¹³. The application of these techniques has been limited by its shortcomings.

In this paper use of Pumice, which is a lightweight volcanic rock has been discussed as an adsorbent for fluoride removal from water. Pumice has been used in the past by researchers also for fluoride removal and has been established as a potent adsorbent because of its large surface area, 90% porosity and ease of availability in nature. Pumice is known to have a low density as a result of the formation of cavities and cells due to gas expansion which results in the release of pressure. The removal efficiency of fluoride from drinking water by using pristine pumice as an adsorbent and its variation with sorbent dose, contact time and initial fluoride concentration has been discussed.

EXPERIMENTAL

Chemicals

The chemicals used in this study were of analytical grade. The experiment was conducted at 25°C with a steady agitation speed of 120 rpm. In order to achieve a stock solution of 100 mg/litre, 221 mg of NaF was added to 1 litre of deionized water. Standard solutions of appropriate concentrations were obtained by serially diluting the stock solution. Pumice Stone powder was procured from a local drug store in Delhi, India. The composition of Pumice is given in Table-2.

Preparation of Pumice

The Pumice Stone powder was washed with distilled water to remove dust. Further, the mixture was heated at 105°C for 24 hours in a hot air furnace to achieve a constant weight.

Table-2: Composition of Pumice¹⁴

Constituent	Percentage (%)
SiO ₂	61.5
Al ₂ O ₃	15.49
CaO	5.9
MgO	2.65
Fe ₂ O ₃	8.4
K ₂ O	1.65
LOI (lost of ignition)	1.59

Batch Adsorption Study

Variation of Fluoride with Time

The effect of time on the amount of fluoride removal was assessed by making use of a fluoride spiked solution of 11mg/litre. Pumice in the dosage of 2g/100mL at a neutral pH was added to the solution. The resultant solution was kept in a shaker at 120 rpm and the fluoride concentration was recorded at an interval of 30 minutes.

Variation of Fluoride with Sorbent Dosage

The impact of sorbent dose on fluoride concentration was carried out by varying the amount of Pumice mixed with the standard solution of 11 mg/litre. The quantity of Pumice powder was kept as 2g/100mL, 3g/100 mL, 4g/100 mL, and 5g/100mL for 150 minutes at pH 7.

Variation with a Concentration of Fluoride

The effect on removal efficiency due to the fluoride initially present in water was analyzed by preparing standard solutions of working concentration (8, 9, 10, 11 and 12 mg/litre). The fluoride in resultant solutions was examined at a neutral pH after a contact time of 150 minutes.

$$\text{Removal Efficiency (E)} = \frac{[\text{Initial fluoride (ppm)} - \text{Fluoride (ppm)}] * 100}{\text{Initial fluoride (ppm)}} \quad (1)$$

RESULTS AND DISCUSSION

Impact of Contact Time on Removal Efficiency

The variance of the amount of fluoride with the residence time is depicted in Fig.-1. It has been found that with an increase in the contact time, the amount of fluoride adsorbed has increases when the pumice dosage was kept constant and agitation speed was set at 120 rpm. There was a gradual increase in efficiency from 19.09% at 30 minutes to 25.45% at 150 minutes. The advancement in removal efficiency was on the virtue of access to the adsorbent spots and dispersion of adsorbent particles in the solution. There was a hike in efficacy at 30 minutes but as time progressed; the performance was not significant due to the saturation of active sites.

Impact of the Sorbent Dosage on Removal Efficiency

The outcome of Pumice dosage on fluoride spiked solution is illustrated by Fig.-2. The results demonstrated that the fluoride ingested by Pumice is directly proportional to the amount of Pumice in the solution. The increasing adsorbent dosage contributes to a greater number of active sites in the solution which further induces a change in the removal efficiency¹⁵. When the Pumice dosage was varied from 2g/100mL to 5g/100mL, there was an upsurge in removal efficiency from 25.45% to 42.72%. However, the increase in percentage removal after 4g/100mL is lower as compared to the increase in percentage removal when the adsorbent dose exceeded 3g/100mL. This is on the account of the formation of a monolayer of fluoride on the adsorbent surface, shielding affect and agglomeration of adsorbent particles.¹⁶

Impact of the Initial Concentration of Fluoride on Removal Efficiency

There was an indirect relationship between the initial concentration of fluoride and the removal percentage, which is portrayed in Fig.-3. As the initial concentration of fluoride began to rise, the removal performance

declined with constant pH, temperature, agitation speed and Pumice dose. When the initial strength was 8 mg/litre, the percentage of extracted fluoride was found to be 30% and when the initial dosage of fluoride rose to 12 mg/litre, the efficacy depreciated to 20%. At lower fluoride concentration, access to a greater number of active spots on the adsorbent leads to a higher removal percentage of fluoride. The fall in efficiency is attributed to increasing fluoride concentration. At a higher initial concentration, the fluoride ions compete for the active spots which leads to a fall in the removal efficiency.

Fig.-1: Impact of Time on Removal Efficiency (11mg/litre Fluoride Solution, Temperature 25°C, Neutral pH, 2g/100mL Sorbent Dose)

Fig.-2: Impact of Sorbent Dosage on Removal Efficiency (11mg/litre Fluoride Solution, Temperature 25°C, Neutral pH)

Fig.-3: Impact of Initial Fluoride Concentration on Removal Efficiency (2g/100mL Sorbent Dose, Temperature 25°C, Neutral pH)

Adsorption Isotherms

In this study, Langmuir and Freundlich's Isotherms were plotted. By plotting a graph between $\frac{C_e}{q_e}$ and C_e , the value of R^2 was determined. The general equation of Langmuir Isotherm is given by:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m K_L}\right) + C_e \left(\frac{1}{q_m}\right) \quad (2)$$

The R^2 value was maximum for Langmuir Isotherm, which was 0.9869. Hence, it was inferred that the adsorption of fluoride on Pumice follows Langmuir Isotherm. Separation factor, R_L in the case of Langmuir Isotherm indicates whether the isotherm is favourable or not favourable. It is represented by the equation-3.¹⁷

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

Table-3: Values of Separation Factor

Value of R_L	Isotherm
$R_L > 1$	Not Favorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Fig.-4: Langmuir Adsorption Isotherm

CONCLUSION

Following conclusions are drawn from the study:

- Pristine Pumice can be utilized to extract fluoride effectively from the fluoride contaminated solution on the virtue of its ease of availability and low cost.
- The effectiveness of Pumice as an adsorbent is determined by the actual fluoride concentration in the water, sorbent dosage and the duration for which Pumice is in contact with the solution.
- A direct relationship between contact time and the percentage of fluoride removal was witnessed. As the contact time increased, the ability of Pumice to adsorb fluoride was enhanced. When the reaction time was varied from 30 minutes to 150 minutes, the removal capacity gradually increased from 19.09% to 25.45%. The removal efficiency was also a function of sorbent dosage. The efficiency experienced a rise when the sorbent dosed was increased. The removal percentage advanced from 25.45% to 42.72% when the sorbent dosed was varied from 2g/100mL to 5g/100mL.
- With a rise in the initial concentration of fluoride in water, the removal percentage was observed to decrease. The reduction rate fell from 30% to 20% as the strength of fluoride solution increased from 8mg/liter to 12mg/liter.
- R_L value for Langmuir Isotherm was 0.013 which indicated that the isotherm was favorable.

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