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Fluoride Removal from Drinking Water Using Used Tea Leaves as Adsorbent

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Fluoride concentration in drinking water above 1.5 ppm creates health hazards. In the present investigation the removal of fluoride has been attempted using used tea leaves obtained from college canteen. Characterization studies of used tea leaves were carried out by standard procedures (ISI 1989 and APHA 1995). Used tea leaves were treated chemically and digested in alum. The fluoride removal studies were done by adsorption method on used tea leaves. The effects of contact time, pH and adsorbent dose were investigated. The fluoride removal process confirms to second order kinetics. The adsorption followed Langmuir isotherm. The results show that the adsorption capacity of the adsorbent used tea leaves was found to be 0.253 mg/g. Regeneration is effective using 2 % alum solution in the column.

Key Words: Fluoride removal, Used tea leaves, SPADNS, Adsorption isotherms, Column.

INTRODUCTION

Pure water is scarce and is not easily available to all human being. Deprived sections of the society consume contaminated water and take ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents[1]. One such contaminant is fluoride.

Fluorine (F_2) is a greenish diatomic gas and highly reactive that it is never encountered in its elemental gaseous state except in some industrial processes. The fluoride occurs notably as sellaite, fluorspar, cryolite, fluorapatite, villianmite and bastnaesite[2]. Consumption of excess fluoride from drinking water causes fluorosis, a dangerous disease which is characterized by mottled teeth in dental fluorosis and brittle bones in severe skeletal fluorosis[3]. The fluorosis is caused by oral intake of fluoride when drinking water contains more than the permitted concentration of fluoride (1.5 mg/L).

Defluoridation is normally accomplished by precipitation (coagulation) and adsorptive processes[4-12]. Fluoride removal by chemical precipitation using alum, iron, lime and magnesium compounds was investigated by several researchers and reported requirement of high doses of alum[13-15].

Sequential addition of lime, bleaching powder (for disinfection) and alum or aluminium chloride known as the Nalagonda technique is found effective[16], economic and is extensively used in India for defluoridation of community water supplies. But it has some problems associated with operation and sludge disposal. In this respect removal of fluoride by adsorption onto low-cost materials like limestone, kaolinite, bentonite, charfines, lignits and nirmali (strychnos potatorium) seeds extract, bone char, serpentine and sulfonated saw-dust carbon are of limited scope[17-26].

This study presents the findings of an investigation on the use of waste tea leaves for the defluoridation of water by conducting batch studies and continuous down-flow column studies[27-29].

EXPERIMENTAL

Used tea leaves collected from local canteen was cleaned with hot water (*ca.* 80 ºC) to remove sugar and milk sticking on the surface of used tea leaves. The washed tea leaves were sun dried to remove moisture. Using Retsch AS 200 Analytical Sieve Shaker particles of size in the range 250-500 µm (average size of 375 µm) were separated. The over sized used tea leaves were ground by a mortar and pestle and again sieved to get the required size of tea leaves.

Chemical treatment to used tea leaves was given by taking 10 g of tea leaves and adding 100 mL of 0.4 N H_2SO_4 and 20 mL of 30 % formaldehyde. This mixture was kept on a hot plate with a constant temperature of 50 ºC for 3 h. Then the tea leaves were washed with distilled water for many times to remove the acid and formaldehyde. Then they were kept in a hot air oven to remove the moisture. Then it was digested in 2 % alum solution. This was designated as used tea leaves chemically treated with sulphuric acid and formaldehyde.

A stock solution of NaF (5 mg/L) was prepared and this was used throughout the experiments. The adsorption experiments at room temperature were performed by mixing used tea leaves with 100 mL of NaF in Eltech Magnetic stirrer MS203. The residual fluoride concentration in each sample was determined by SPADNS method[30], outlined in the standard methods for examination of water and waste water (APHA 1995) using a spectrochem MK-II spectrophotometer.

Batch experiments were conducted using used tea leaves impregnated with alum in neutral aqueous medium. The extent of adsorption on used tea leaves was also evaluated. The effects of contact time on defluoridation were studied for 30, 60, 90, 120, 150 and 180 min. The extent of adsorption with the variation of pH from 1-8 were also determined. The pH of the solution was measured with Elico India L1 pH meter. The pH was varied using dilute HCl and NaOH solution. The extent of adsorption with the variation of adsorbent dose (8, 10, 12 and 14 g/L) were also determined.

In column experiments, by varying the flow rate and bed depth, effect of bed depth, effect of flow rate, breakthrough characteristics and fluoride removal efficiency for ground water were determined. Column experiments were done in a packed column of diameter 3 cm and height of 45 cm with inlet arrangements to allow fluoride solution to flow through the adsorbent used tea leaves. The over head tank is of 15 L capacity.

The column was packed with the adsorbent used tea leaves for different bed depth 7, 10.5 and 14 cm. Packing was done gradually and compact. Fluoride test solution was allowed to flow through the column bed at a determined flow rate. The outlet was analyzed for fluoride content.

RESULTS AND DISCUSSION

Characterization of used tea leaves: Characterization studies were carried out by standard procedures (ISI 1989 and APHA 1995). The results are presented in Table-1.

TABLE-1
CHARACTERISTICS OF USED TEA LEAVES

Characteristics	Value
pH	6.48
Moisture content (%)	2.52
Ash content (%)	6.07
Water soluble matter (%)	2.8
Acid soluble matter (%)	4.24
Apparent density (g/cc)	0.25
Decolorizing power (mg/g)	9
Iodine value (mg/g)	1040
Phenol number (mg/L)	90
Ion exchange capacity (meq/g)	0.4

Sorption studies: Knowledge of the optimal conditions would herald a better design and modeling adsorption process. Thus the effect of some major parameters like pH, contact time and adsorbent was investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the rate and equilibrium data. Experiments were carried out by shaking 0.5 g of adsorbent dose with 100 mL of aqueous solution containing known concentration of fluoride ions and by agitating the samples on Eltech Magnetic stirrer MS203. All experiments were conducted at room temperature.

Effect of pH on fluoride removal: The influence of pH on removal of fluoride studied employing test solutions adjusted to initial pH values of 8.00 ± 0.10, 7.00 ± 0.10, 6.00 ± 0.10, 5.00 ± 0.10, 4.00 ± 0.10, 3.00 ± 0.10, 2.00 ± 0.10, 1.00 ± 0.10. The results are shown in Table-2 shows the effect of pH. As the pH of the test fluoride solution is increased from 1-8 removal of fluoride remains more or less constant at around 88-90 % up to a pH of 6 but greatly reduces to 59 % at a pH 8. Hence for further studies the pH was maintained at 6.

TABLE-2
EFFECT OF pH ON FLUORIDE REMOVAL

pH	Absorbance	Concentration (ppm)	Fluoride removal (%)
1	0.050	0.50	90
2	0.055	0.55	89
3	0.055	0.55	89
4	0.065	0.55	89
5	0.060	0.60	88
6	0.060	0.60	88
7	0.145	1.45	71
8	0.205	2.05	59

Effect of contact time on fluoride removal: It is found that the removal of fluoride ions increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. The saturation is reached in 150 min (Table-3). For further optimization of other parameters, this contact time was considered as the equilibrium time.

TABLE-3
EFFECT OF CONTACT TIME ON FLUORIDE REMOVAL

Contact time (min)	Absorbance	Concentration (ppm)	Fluoride removal (%)
5	0.360	3.60	28
30	0.245	2.45	51
60	0.160	1.60	68
90	0.115	1.15	77
120	0.070	0.70	86
150	0.045	0.45	91
180	0.045	0.45	91
200	0.045	0.45	91

Effect of adsorbent dose on fluoride removal: Removal of fluoride from water increased with an increase in the dose of used tea leaves and the experimental results are presented in Table-4. It follows from the figure that fluoride uptake increased as the dose of used tea leaves is increased from 1 g/L (33 %) to 12 g/L (90 %) to 16 g/L (92 %). At higher doses of the adsorbent, more sorbent surface will be available for the sorption reaction and this resulted in higher removal. It may also be observed that initially the removal of fluoride increases as the dose is increased, but beyond certain dose range, there is no significant increase in removal. This may be due to exhaustion *i.e.*, non-availability of fluoride ions or even due to non sorbability of fluoride ions as a result of sorbent-sorbate interaction.

TABLE-5
ADSORPTION ISOTHERM CALCULATION FOR USED TEA LEAVES-FREUNDLICH AND LANGMUIR ISOTHERM

S. No.	Initial conc. (mg/L)	Equilibrium concentration 'C' (mg/L)	Uptake, 'Q' (mg/g)	Freundlich isotherm		Langmuir isotherm	
				ln C	ln Q	1/C	1/Q
1	5.0	0.63	0.35	-0.400	-1.040	1.58	2.85
2	7.5	0.90	0.51	-0.100	-0.670	1.11	1.96
3	10.0	1.01	0.69	0.009	-0.370	0.99	1.44
4	12.5	1.10	0.89	0.095	-0.110	0.90	1.12
5	15.0	1.27	1.09	0.240	0.086	0.787	0.91

TABLE-4
EFFECT OF ADSORBENT DOSE ON FLUORIDE REMOVAL

Adsorbent dosage (g/L)	Absorbance	Concentration (ppm)	Fluoride removal (%)
1	0.335	3.35	33
2	0.270	2.70	46
5	0.210	2.10	58
8	0.135	1.35	73
10	0.075	0.75	85
12	0.050	0.50	90
14	0.045	0.45	91
16	0.040	0.40	92

Sorption mechanism: The sorption data (Table-5) for the removal of fluoride ions have been correlated with Freundlich and Langmuir models. From the data, it is found that Langmuir model fits the process of defloridation using used tea leaves well.

Column studies with used tea leaves: To investigate the practical aspects of application of used tea leaves for removal of fluoride from water, dynamic down-flow column studies were conducted. Effect of bed depth and effect of flow rate are studied.

Effect of bed depth: By keeping the flow rate constant at 5 mL/min, pH at 6 and initial fluoride concentration 5 mg/L the effect of bed depth or the breakthrough point was studied for three different bed depths (7, 10.5 and 14 cm). The breakthrough occurred at 550 mL for a bed depth of 7 cm, 1150 mL for 10.5 cm and 2000 mL for 14 cm. Data show that the breakthrough point increased with increase in bed depth (Table-6 and Fig. 1).

TABLE-6
FLUORIDE REMOVAL CAPACITIES FOR DIFFERENT BED DEPTHS FOR USED TEA LEAVES

Time (min)	Water collected (mL)	Final conc. (mg/L)	Fluoride removal (mg)
Adsorbent weight = 10 g, Bed depth = 7 cm			
20	100	0.0	0.50
50	250	0.5	1.13
70	350	1.0	1.53
110	550	1.5	2.23
Adsorbent weight = 15 g, bed depth = 0.5 cm			
90	450	0.0	2.25
180	900	0.5	4.28
200	1000	1.0	4.68
230	1150	1.5	5.20
Adsorbent weight = 20 g, bed depth = 14 cm			
210	1050	0.0	5.25
340	1700	0.5	8.18
370	1850	1.0	8.78
400	2000	1.5	9.30

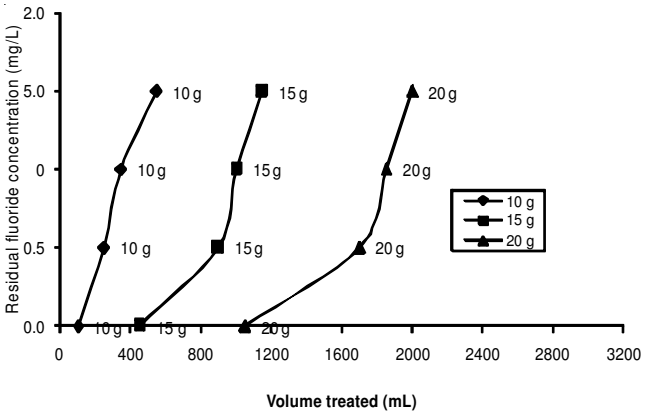

Fig. 1. Breakthrough curves for different bed depths for used tea leaves

Effect of flow rate: By keeping the bed depth constant at 10.5 cm pH at 6 and initial fluoride concentration 5 mg/L the effect of flow rate on breakthrough time was studied for different flow rates (5, 10 and 15 mL/min). The breakthrough occurred at 1150 mL for a flow rate of 5 mL/min, 700 mL for 10 mL/min and 600 mL for 15 mL/min. Table-7 shows clearly that the breakthrough point decreased with increase in flow rate.

TABLE-7
FLUORIDE REMOVAL CAPACITIES FOR DIFFERENT FLOW RATE FOR USED TEA LEAVES

Time (min)	Water collected (mL)	Final conc. (mg/L)	Fluoride removal (mg)
Rate of flow = 5 mL/min			
90	450	0.0	2.25
180	900	0.5	4.28
200	1000	1.0	4.68
230	1150	1.5	5.20
Rate of flow = 10 mL/min			
30	300	0.0	1.50
50	500	0.5	2.25
60	600	1.0	2.40
70	700	1.5	2.45
Rate of flow = 10 mL/min			
30	300	0.0	1.50
50	500	0.5	2.25
60	600	1.0	2.40
70	700	1.5	2.45
Rate of flow = 15 mL/min			
10	150	0.0	0.75
20	300	0.5	4.13
30	450	1.0	2.03
40	600	1.5	2.55

Regeneration studies: Regeneration was done by passing 2 % alum solution at a flow rate of 2 mL/min for 6 h.

Conclusion

Results show that used tea leaves could be fruitfully used for the removal of fluoride over a wide range of concentrations. Batch studies indicate that for an optimum adsorbent dose of 12 g/L and 5 mg/L of initial fluoride concentration at 6 pH and contact time 150 min the fluoride removal was about 91 %. Data obtained for isotherm confirmed to Langmuir isotherm for used tea leaves. The adsorption capacity of used tea leaves was found to be 0.253 mg/g for an initial fluoride concentration of 5 mg/L. The fluoride removal process confirms to second order kinetics. The capacity of used tea leaves was found to be 0.223, 0.347 and 0.465 mg/g corresponding to bed depths 7, 10.5 and 14 cm.

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