

Ion Selective Electrode Determination and Removal of Fluoride ions Using Starch Derivatives as Adsorbents from Groundwater Samples of Barmer District

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Abstract: The evaluation of groundwater quality is a critical element in the assessment of water resources and this analysis becomes even more important when used for determining concentration of toxic anion, like fluoride. In the present investigation, firstly, samples of groundwater were collected from various sites of Barmer (an arid district of western Rajasthan). Fluoride ion concentrations were then determined in these samples using suitable ion electrodes and further the use of quarternary aminised resins from starch as adsorbents was evaluated using Freundlich adsorption isotherm for removal of fluoride.

Keywords: Fluoride, determination, removal, starch, water analysis

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I. INTRODUCTION

Groundwater contamination by fluoride (F⁻) results mainly from the dissolution of minerals from subterranean strata^{1,2}. Though small amount of fluoride is vital for humans but it is toxic when present in large amounts. According to World Health Organization, the maximum acceptable concentration of fluoride in drinking water lies below 1.5 mg/L (WHO, 2004). When fluoride present is more than 1.5 mg/L, it causes mottling of teeth and lesions in thyroid gland, liver and other organs^{3,4}. The effect of prolonged use of fluoride containing water on human health is shown in Table-1.

Table 1: Effect of prolonged use of fluoride containing water on human health

F ⁻ mg/L	Health outcome
< 0.5	Dental caries
0.5-1.5	Optimum dental health
1.5-4.0	Dental fluorosis
4.0-10.0	Dental and skeletal fluorosis
>10.0	Crippling fluorosis

The most common symptoms of chronic fluoride exposures are dental fluorosis and skeletal fluorosis. In dental fluorosis, the structural integrity of enamel is affected and small pits are left in teeth as it breaks away and in skeletal fluorosis there occurs accumulation of fluoride in skeletal tissues. The common fluoride bearing minerals found in soil are fluorspar (CaF₂), cryolite (Na₃AlF₆) and chilotite (Na₅Al₃F₁₄)⁵. Fluoride displaces hydroxide ion from hydroxyapatite, Ca₅(PO₄)₃OH, the principal mineral constituent of teeth (enamel) and bones to form the harder and tougher fluoroapatite, Ca₅(PO₄)₃F. Upto small levels it strengthens the enamel, however, at high fluoride concentrations the conversion of a large amount of hydroxyl apatite to fluoroapatite makes teeth and bones (after prolonged intake) denser, harder and more brittle. This causes mottling and embrittlement of teeth (dental fluorosis) and after a prolonged exposure of fluoride this progresses into skeletal fluorosis (Table-1). Fluoride is thus considered beneficial in drinking water at low concentration (about 0.7 mg/L) only, but harmful when exceeds 1.5 mg/L⁶. It was estimated (WHO, 1984) that more than 260 million people worldwide are consuming drinking water with fluoride content > 1.0 mg/L. The excess level of fluoride in drinking water is becoming a matter of great concern. This concern is more serious in countries where ground water is used as a main water supply resource. Several defluoridation methods based on the adsorption, precipitation & ion exchange resins have been developed during last four decades, however, none of these could solve this problem at a completely acceptable level⁷.

Considering the potential risks imposed on human health by presence of excess of fluoride ions in drinking water the present study was carried out to determine fluoride contents in ground water samples from various blocks of Barmer district (Rajasthan, India) potentiometrically using ion selective electrodes and preliminary studies on application of quarternary aminised resins from starch as adsorbents for removal of fluoride were also carried out.

II. MATERIAL AND METHODS

Materials: All the reagents and chemicals used in this study are commercially available and are of high purity AR grade. Analysis of fluoride was performed using fluoride ion selective electrode. Double distilled water (Millipore) was used throughout the experiments. Fluoride stock solutions (1000 ppm) were prepared from sodium fluoride and stored in polyethylene containers. Total ionic strength adjustment buffer (TISAB) solution containing 58 gm of NaCl, 57 ml of glacial acetic acid, 4 gm of 1,2- cyclohexanediamine – N,N,N',N'-tetraacetic acid (CDTA) and approximately 150 ml of 6 M NaOH in a volume of 1000ml (Ph 5.0-5.5)^{8,9} was used to regulate the ionic strength of samples and standard solution, to adjust the pH and also avoid interferences by polyvalent cations such as Al(III), Fe(III) and Si(IV) which are able to complex or precipitate with fluoride and reduce the free fluoride concentration in the solution. CDTA forms more stable complexes with polyvalent metal cations than metal-fluoride complexes (AlF_6^{3-} , FeF_6^{3-} , etc.) in solutions. CDTA forms metal-CDTA complexes in a metal-ligand ratio of 1:1¹⁰, freeing the fluoride ion. The electrode is selective for fluoride ion over other common anions by several orders of magnitude, only the hydroxide ion appears to offer some interference.

The adsorbents used in this study are cross linked starch derivatives, namely Glycidyl Trimethyl Ammonium Chloride (GTMAC) & Glycidyl Triethyl Ammonium Chloride (GTEAC) and diethyl amino-ethyl-starch referred onward as GTMAC-, GTMEC- & DEAE- Starch respectively. These were prepared by mixing cross linked starch and GTMAC, GTMEC and DEAE in the ratio of 2:1 in chlorine form. The mixture was kept at 60 °C with constant stirring for two hrs. The products were brought to room temperature where they were kept for 6-8 hours and then filtered. The physical properties of starch derivatives viz. degree of substitution, particle size, water regain, salt splitting capacity, exchange capacity, swelling and stability were evaluated by known methods. These are reported in Table 2.

Table 2: Physical properties of starch derivatives

S. No.	Derivatives	Particle Size %	Mesh	Degree of Substitution %	Water Regain g/g	Salt Splitting Capacity Meg/g	Weak Exchange Capacity
1.	GTMAC-S	60	40-60	0.27	2.26	0.62±0.04	0.25+0.05
		40	>60				
2.	GTMEC- S	60	40-60	0.27	2.32	0.34±0.02	0.21+0.05
		40	>60				
3.	DEAE- S	60	40-60	0.23	2.42	0.29±0.03	0.20+0.07
		40	>60				
Stability: 6-8 weeks at pH 3- 10							
Swelling in water: slightly							

Methods: About 27 ground water samples were collected from different blocks/areas of Barmer district (Rajasthan, India). All the samples were collected from deep-wells and hand-pumps. These samples were transported to environmental laboratory, Department of Chemistry, J.N.V. University, Jodhpur where fluoride analysis was performed immediately.

The development of ion-selective electrodes (ISE) makes possible the determination of the concentration of ions of choice greater selectivity and sensitivity using electrode membranes. Therefore, ion selective electrodes were used to determine fluoride concentrations in ground water samples. The samples and fluoride standard solutions were diluted 1:1 with the TISAB. The solution which contains 20 ml of TISAB and 20 ml of sample, were mixed with a magnetic stirrer for 5 min.

The batch technique was selected to obtain the equilibrium and kinetic data. The uptake of fluoride on the adsorbent was estimated in terms of distribution coefficient or adsorption capacity, K_d . The derivatives (0.04-0.2 g) were stirred with 100 ml of 0.02 g dm⁻³ aqueous solution of samples at pH 7-8, in skew cap jars until complete equilibrium was obtained. The agitation was continued for 30 min. at ambient temperature (30 ± 2 °C) The equilibrated solutions were shaken in a thermostat shaker at speed of 300 RPM. The adsorbent was then removed by filtration through glass wool and the residual [F⁻] in the solution was determined using ion selective electrodes.

III. RESULTS AND DISCUSSIONS

The fluoride concentrations in ground water samples collected from different locations are tabulated in Table 3. The Figure 1 indicates the variation for fluoride ion concentrations at various sampling sites.

Table 3: Fluoride concentrations in ground water samples from various locations in Barmer district

Sample location	Sample location	F ⁻ concentration (mg /L)
S1	Sarwari	3.65
S2	Tarsinghri	0.306
S3	Gharsikabara - 1	0.120
S4	Gharsikabara -2	0.161
S5	Pataukala	1.69
S6	Pataukhurd	0.136
S7	Kuri	0.119
S8	Bhandiyawas	0.622
S9	Pachpadra	3.15
S10	Bithuja	0.692
S11	Bhagundi	0.228
S12	Akarlibakshiram	0.740
S13	Sambhara	0.448
S14	Lakhekiberi	0.802
S15	Khara par	3.10
S16	Tilwara	0.282
S17	Kher temple	0.516
S18	Badu kabara	2.02
S19	Kudi	0.250
S20	Bhandiyawas -1	0.622
S21	Bhandiyawas -2	0.843
S22	Bhanduyawas-3	0.822
S23	Borawas	0.680
S24	Bhagundi	2.83
S25	Khara par -1	2.15
S26	Khara par-2	0.194
S27	Kuri deep well	0.215

The analysis of ground water being collected from different areas of Barmer district revealed that out of 27 samples, high fluoride level was obtained at Sarwari, Patau Kala, Pachpadra, Khara Par and Bhagundi sampling areas. The water of these regions probably passes through soil or rock layers rich in fluoride in comparison to other regions. The concentration of fluoride in ground water depends on various factors such as geological, chemical, consistency of soil, porosity of rocks, pH, temperature and depth of wells.

Some locations like Tarsingri, Gharsika Bara, Patau Khurd and Kuri had insufficient fluoride content with an average of about of 0.168 mg/L.

The efficiency of starch derivatives for the removal of F⁻ from water was evaluated using Freundlich isotherm. The linear plot of Log Q_e Vs Log C_e indicated that all the starch derivatives had good affinity for fluoride removal and order of adsorption for fluoride ions towards the derivatives was GTMAC-S > GTMEC-S > DEAE-S.

The constant values of K_d and 1/n are a measure of adsorption capacity and adsorption intensity, respectively. These constants are given in table 4. Values of 1/n lying between 0 and 1 and values of n lying in the range of 1-10 confirmed the favorable conditions for adsorption.

Figure-1: Variation in Fluoride ion concentration (mg/L) at various sampling sites of Barmer district

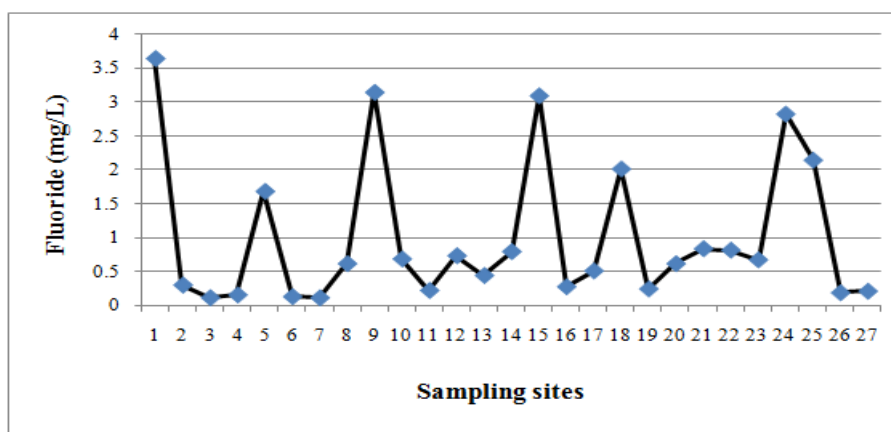


Table 4: Freundlich constants for the adsorption of fluoride ion on starch derivatives

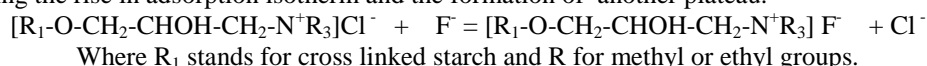
[F]	= 0.02 g dm ⁻³						
Time of Contact	= 30 min						
Adsorbent	= 0.15 g						
Temperature	= 30 °C						
Volume	= 0.1 dm ³						
pH	= 8						
Adsorbent	Freundlich Constants						
	Average k_d	K	n	1/n	SD	R ²	r
GTMAC- S	2135±50	3.459×10 ⁻³	2.52	0.396	1.06×10 ⁻²	0.99	0.99
GTMEC-S	1580±70	2.887×10 ⁻³	2.60	0.385	2.15×10 ⁻²	0.99	0.97
DEAE-S	1782±50	2.286×10 ⁻³	3.10	0.322	0.86×10 ⁻²	0.98	0.99

The results also indicate that the K_d values increase with the decrease in pH of solution, which may be attributed to the neutralization of surface negative charge of Starch derivatives.

Adsorption Isotherms (AI) for fluoride ions in water on starch derivatives when the system was in equilibrium were found regular, positive and convex to the concentration axis followed by a plateau and another rise and formation of plateau. The sharp rise of isotherms in the initial stages of low equilibrium concentration indicated that there are plenty of readily available sites for fluoride ion. Eventually a plateau was reached in all the three cases, which indicated the saturation of adsorbent surface at this stage. Further rise in the adsorption isotherms and the formation of another plateau probably indicates mono dispersity of adsorption accompanied by the formation of small sized ionic micelles on the surface. A similar behavior has been observed in the adsorption of merocynine over silver halides.

The experimental data was analyzed in the light of Freundlich equation¹⁰ to predict the nature of adsorption. The plots of $\log C_e$ against $\log x/m$ were found linear yielding an intercept on the ordinate. The Freundlich constants K_d and $1/n$ were calculated from the intercept and slope of these curves using computerized LRG program and reported in Table 4. The extent of adsorption, n , was found in the range of 2.52 to 3.1, which is quite satisfactory.

The mechanism of adsorption may be considered as a mixed effect of classical as well as of chromatographic adsorption. The introduction of glycedyl trialkyl ammonium groups in the starch derivatives imparts it a strongly cationic anion exchanger's character. Initially all the Cl^- ions of the GTMAC-Starch were exchanged by F^- ions with the formation of first plateau, after the saturation point was reached i.e. the capacity of ion exchanger was exhausted the F^- ions were then held by hydrogen bonding and weak Vander Waal's forces showing the rise in adsorption isotherm and the formation of another plateau.



Starch is basically a storage polysaccharide of plants which acquires a negative surface charge by virtue of primary hydroxyls on each D-glucopyranose units. The alkaline treatment of starch, during the introduction of quaternary ammonium group, causes degradation of about 2 % with the loosening of the structure and the introduction of some acidic sites which do contribute to negative charge. In acidic media the

primary hydroxyls on the D-glucopyranose units may get protonated acquiring a partial positive charge which helps the fluoride ions to move in the vicinity of the starch molecule where hydrogen bonding comes into play and the fluoride ion is held by hydrogen bonding, resulting in the increased adsorption after exhausting the anion exchange capacity.

IV. CONCLUSION

Salient features of the presented research work are:

1. The above presented research work has provided empirical data about F⁻ ions in ground water of the Thar desert regions of Barmer district, which indicates that ground water of some area of Barmer district is not suitable for drinking purpose and therefore proper management plans must be adopted to control F⁻ ion concentrations in them.
2. The present study demonstrates that the cationic Starch derivatives have potential to remove fluoride from drinking water without any other toxic affect.
3. The uptake of fluoride ion is rapid in initial stages and decreases gradually while approaching equilibrium.
4. The material after the use can be burnt, thus pose no waste disposal problem.

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