REMOVAL OF FLUORIDE FROM WATER USING LOW-COST MATERIALS

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ABSTRACT

This paper presents the results of investigations carried out for removal of Fluoride from water employing physico-chemical processes of adsorption and coagulation employing abundantly available and low-cost materials like Rice Husk, seed extracts of Moringa Oleifera (Drum stick), and chemicals like Manganese Sulphate and Manganese Chloride. Rice husk of 6g/l accomplished a removal of 83% of Fluoride from a 5mg/l of Fluoride solution requiring an equilibrium time of 3 hours. Equilibrium Isothermal data fitted well into rearranged linearised Langmuir adsorption model. Fixed bed down flow column studies demonstrated the practical utility of Rice husk. Standard Jar Tests conducted with *Moringa oleifera seed extracts* (MOE), Manganese Sulphate and Manganese Chloride accomplished removal percentages of 92, 92, 94 and 91 of Fluoride from a 5mg/l test solution at a dosage of 1000 mg/l. A slightly acidic pH of 6.0 was found favorable for Fluoride removal by Manganese sulphate, Manganese Chloride and MOE.

1.0 INTRODUCTION

Fluoride is a ubiquitous element present in earth's crust and is also being added to the environment anthropogenically. It is the most electronegative of all elements. Fluorine is found in the soil and the content of Fluorine in the lithosphere varies between 100 and 1500 g/ton. Fluoride has gained importance due to its dual influences on human beings. In lower concentrations, Fluoride is an essential nutrient which aids in the formation of bones, prevents tooth decay, etc whereas in higher concentrations it causes fluorosis, brittling of bones, curvature of bones, dwarfishness, mental derangements, cancer, etc. and in extreme cases even death.

It is estimated that around 260 million people worldwide (in 30 countries) are drinking water with Fluoride content more than 1.0 mg/l. In India alone, endemic Fluorosis is thought to affect around one million people and is a major problem in 17 of the 25 states, especially Rajasthan, Andhra Pradesh, Tamil Nadu, Gujarat and Uttar Pradesh.

According to WHO standards, the Fluoride in drinking water should be within a range that slightly varies above and below 1 mg/L (Meenakshi [1]). In temperate regions, where water intake is low, Fluoride level up to 1.5 mg/L is acceptable. The Bureau of Indian Standards, BIS (IS-10500) [2], has prescribed a desirable limit and permissible limit of Fluoride in drinking water as 1.0 and 1.5 mg/l respectively

2.0 Removal of Fluoride from water:

Defluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes. One of the well-known methods called 'Nalgonda Technique' was developed by National Environmental Engineering Research Institute, Nagpur, India (Bulusu, et. al. [3]) is a precipitation processes employing alum followed by sedimentation and/or filtration. It involves the addition in proportions and in sequence of lime/sodium carbonate, alum or aluminum chloride and bleaching powder. The contents are mixed for a brief period and after sedimentation, fluoride free supernatant is used for supply whereas the chemical sludge is withdrawn and disposed off.

Chemical precipitation methods, employing soluble metal salts are associated with certain problems which render them less attractive for field application. In this respect, adsorption and ion exchange processes appear to be a better alternative for field application. Adsorption onto activated carbon, activated alumina, bone char or ion exchange resins has been investigated.

Activated carbon prepared from various raw materials exhibits good fluoride uptake capacity (McKee and Johnston [4]). But the adsorption process is highly pH dependent and is effective at pH less than 3.0 and there is little removal at neutral pH of 7.0. Defluoridation by activated alumina was successfully demonstrated by Boruff [5] and the fluoride removal capacity increases directly with fluoride concentration and inversely with pH of the water Low cost materials like serpentine are effective in removing fluoride from 6.5 mg. L^{-1} fluoride to 1.0 mg. L^{-1} fluoride (Kulkarni and Nawlakhe [6]) but are of limited scope. Activated alumina coated silica gel, activated saw dust, activated coconut shell carbon, coffee Husk, bone charcoal, activated soil sorbent, etc. are some of the different materials investigated for adsorptive removal of Fluoride from water.

Sailaja [7] used Manganese sulphate and Manganese chloride for removal of colour from textile dye C.I. Acid Red 88. Badusha [8] observed that reactive dyes and orange dyes were amenable for chemical treatment (coagulation) with Manganese salts. Srimurali [9] observed removal of more than 95% of colour from different acid, basic and direct dye classes using Manganese salts.

Rice husk contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxy and amidogen, etc. which makes adsorption processes possible (Runping Han, et al. [10]) *Moringa oleifera* consists chemical compounds like 4-(4'-*O*-acetyl-a-L-rhamnopyranosyloxy)benzyl isothiocyanate, 4-(a-L-rhamnopyranosyloxy)benzyl isothiocyanate, niazimicin, pterygospermin, benzyl isothiocyanate, and 4-(a-L-rhamnopyranosyloxy)benzyl glucosinolate and several studies reported on the performance of *Moringa oleifera* seeds as a primary coagulant, coagulant aid and conjunctive with alum (Jed [11]).

The objective of the present study is to investigate the effectiveness of naturally occurring and low-cost materials like Rice Husk and *Moringa olifera* and chemicals like Manganese chloride and Manganese sulphate for removal of Fluorides from water.

3.0 EXPERIMENTAL METHODOLOGY

3.1 Materials: Corning glassware of ‘Pyrex’ quality and analytical reagent grade chemicals were used. The glassware was soaked overnight in a 5.0 mg/L of Fluoride solution to minimize the possibility of Fluoride getting absorbed. The glassware was washed off with nitric acid and distilled water before use. First, a stock solution of 100 mg F/L was prepared by dissolving appropriate amount of sodium fluoride (NaF) in distilled water and desired concentrations of working solutions were then prepared from stock solution. Sulphuric acid (0.1N) and sodium hydroxide (0.1 N) were used for adjusting the pH values either to acidic or alkaline conditions.

Naturally occurring and aundantly available low cost materials like Rice husk, *Moringa Oleifera* seeds were used. Rice husk was obtained from a local mill and was sieved through IS sieves of 150 µm and 300 µm size and the material passing through 150 µm and retained on 300 µm which has a geometric mean size (G_m) of 212 µm was used in all experiments. The apparent density of rice husk is 0.4-0.7 g/cm^3.

Dried *Moringa Oleifera* seeds were obtained locally and kept in an oven at 50^{0}C for 12 hrs. The seeds were made into powder and sieved through 75 µ sieve to get uniform size. In order to obtain an extract of *Moringa Oleifera* nut powder first 10 g of *Moringa* powder was suspended in HCI and NaOH solution of normality (0.5N, 1N, 2N, 3N, 4N and 5N) and observed visually for dissolution of *Moringa Oleifera* powder. It was observed that 0.5N HCI was more effective in dissolving *Moringa Oleifera* powder.

3.2 Experimental Methodology

Agitated, non-flow batch sorption studies were conducted to study the effect of controlling parameters like contact time, sorbent dosage, solution pH etc. Continuous down flow column studies were also conducted to study the practical applicability of rice husk for removal of Fluorides from water. All the experiments were conducted at room temperature (29±2^{0}C). Fluoride concentration was estimated by SPADNS method (APHA[12]) using a SYSTRONICS-105 spectrophotometer.

4.0 RESULTS AND DISCUSSION

4.1 Removal of Fluoride by Rice Husk

4.1.1 Sorption Kinetics

The effect of contact time on removal on Fluoride using Rice Husk is presented graphically as percentage Fluoride removal at different contact times in Figure .1 It may be observed from the Figure that as contact time increases, percent removal also increases initially and reduces gradually with time and attains almost an equilibrium condition in nearly 180 minutes (3 hours) and remains more or less constant thereafter. A maximum of 83 percent removal could be accomplished by Rice Husk. Similar pattern was observed by Nagendra Rao [5], in his investigations on Fluoride removal using the adsorbents of acid treated Bauxite, Lanthanum oxide, Cerium Hydrate and Gamma Alumina

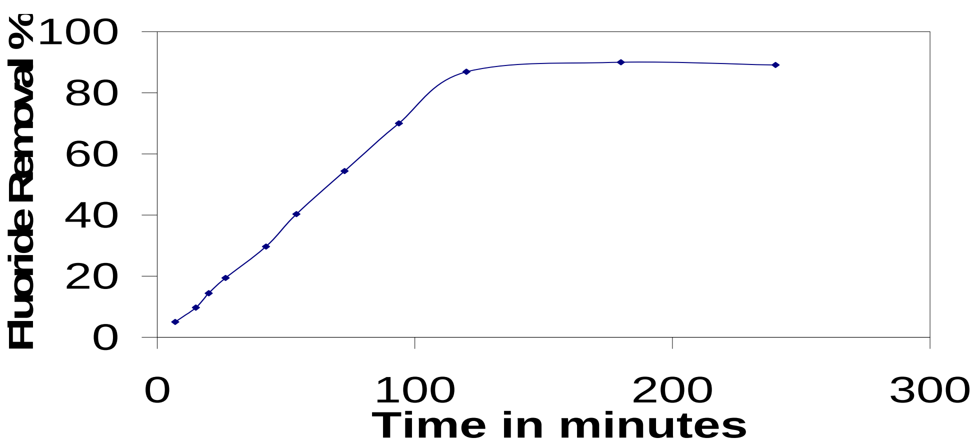

Figure 1. Kinetics of sorption of Fluoride onto Rice Husk

4.1.2 Isotherm equilibrium sorption studies

The values of the sorption capacities and coefficients of correlation (r^2) computed from linearized Langmuir, Freundlich and BET adsorption isotherm equations are given in Table 1

Table 1: Sorption capacities and coefficient of correlation (r^2) for Rice Husk for different Isothermal equilibrium models

S.No	Sorbent	Values of coefficient of correlation (r^2)				
		Langmuir	Freundlich	BET	Q^o	B
1	Rice Husk	0.912	0.825	0.801	0.820	1.142

It is evident from a comparison of the values of coefficient of correlation (r^2) that the equilibrium adsorption of Fluoride on to Rice Husk follows Langmuir adsorption isotherm model which reflects apparent monolayer adsorption on a more or less homogeneous surface of uniform energy levels. The monolayer capacity (Q^o) and adsorption energy (b) were calculated from the linear plot and are also given in Table 1.

4.1.3 Effect of Solution pH

Removal of Fluoride by Rice Husk decreased continuously as pH was increased from 2.0 to 12.0.as depicted in Figure 2. Decrease in removal of Fluoride in pH range of 2.0 to 10.0 was low i.e., 12.8% whereas removal of Fluoride deceased significantly from pH 10.0 to 12.0.

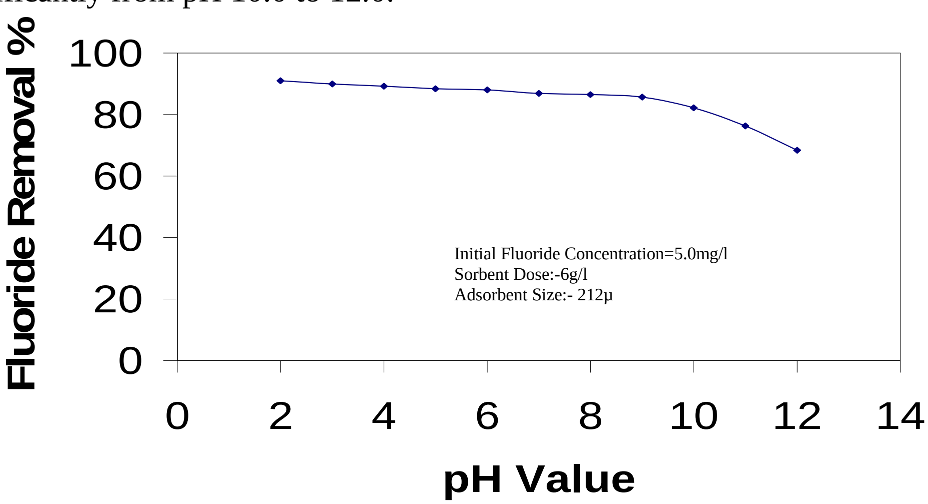

Figure 2. Effect of pH on sorption of Fluoride by Rice Husk

Marginal variation in Fluoride removal by Rice risk over pH range of 2 to 10 indicates its usefulness for removal of Fluoride in the pH range normally encountered in ground waters laden with Fluoride.

4.1.4 Effect of co- and counter ions

Influence of anions like chlorides, sulphates nitrates and carbonates on removal of Fluoride by Rice Husk is depicted in Figure 3.

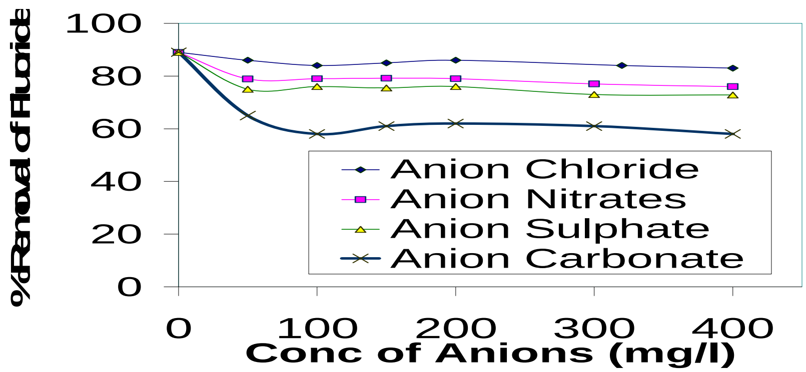

Figure 3. Influence of anions on removal of Fluoride by Rice Husk

The order of reduction in the potential of anions for Fluoride sorption is Carbonates>Nitrates> sulphates>chlorides.

Influence of cations like sodium and magnesium on sorptive removal of Fluoride by Rice Husk is presented in Figure 4.The results indicate that cations sodium and magnesium, have marginal influence of sorptive uptake of Fluoride and the reduction in sorptive uptake ranges from 8%-12%.

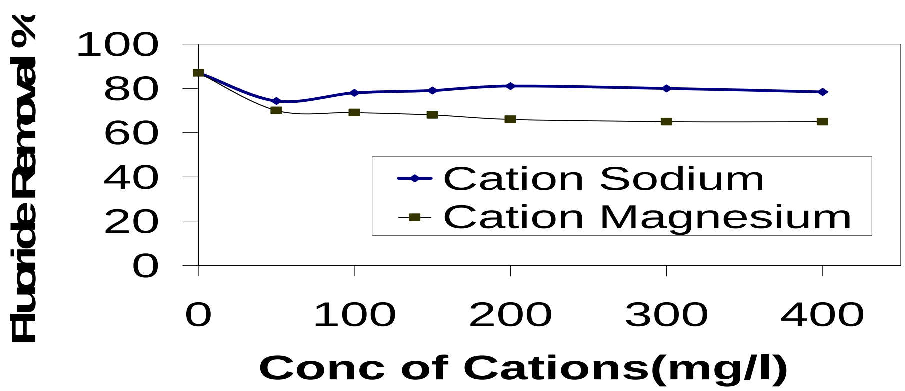

Figure 4. Influence of cations on removal of Fluoride by Rice Husk.

4.1.5 Effect of Sorbent Dose

Results of equilibrium sorption experiments conducted with a test Fluoride solution of concentrations 5.0 mg /l are presented in Figure 5. The amount of Fluoride adsorbed increased with increase in dose and 84% removal was accomplished at a dosage of 6g/L. At higher doses than 6g/L there is no increase in Fluoride removal perhaps due to non absorbability of Fluoride ions.

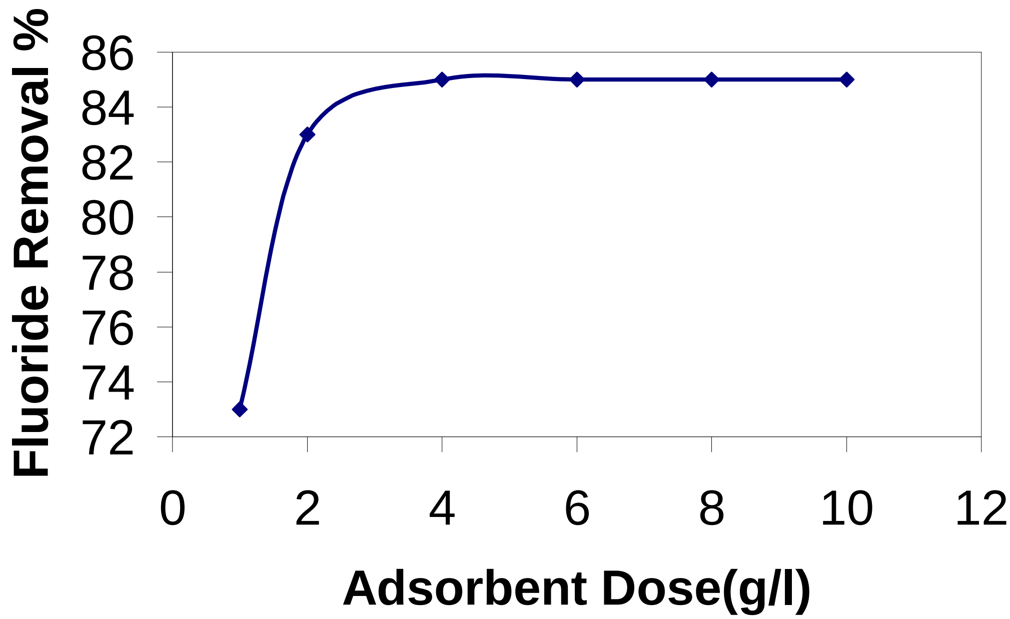

Figure 5. Effect of sorbent dose on Fluoride removal by Rice Husk

4.1.6 Continuous down flow column studies

Test Fluoride solution of 5 mg/L was passed through at different flow rates of 5 ml/minute and 10ml/minute. A break-through curve is obtained by plotting residual Fluoride content on y-axis and time on x-axis and is shown in Figure 6. From the Fluoride removal data, breakthrough time and break through volume were calculated and found as 40 and 22 hours and 12 and 13.2 hours at flow rates of 5 ml/minute and 10ml/minute respectively.

From the break through graph it is evident that the break through curve is a typical S in shape. Fluoride removal was 100% in initial 4 hrs in case of the two flow rates 10ml/mim and 5ml/min. Effluent Fluoride concentration rose to 1mg/l in 8.3 hours in case of the flow rate which was maintained at 10ml/min, whereas for the effluent Fluoride concentration to reach 1mg/l it took 15 hours at a flow rate of 5ml/min. Further to reach 100% exhaustion, it took 13 hours and 40 hours respectively for flow rates of 10ml/min and 5ml/min.

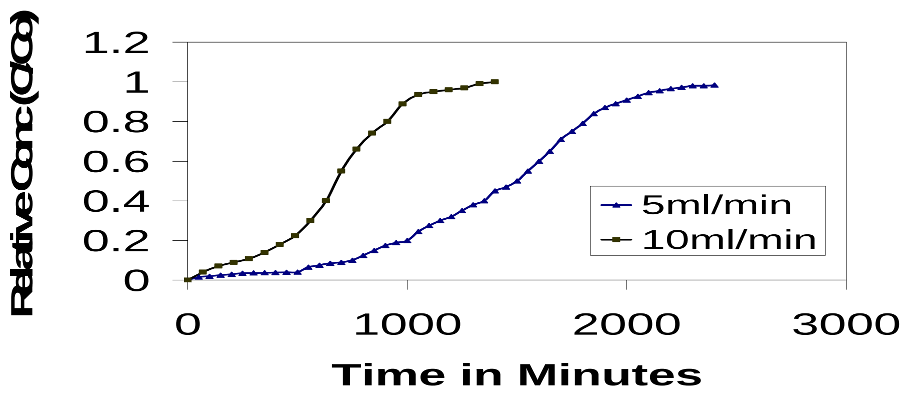

Figure 6. Break through profile for adsorption of Fluoride by column filled with Rice Husk

4.2 Removal of Fluoride by *Moringa oleifera seed Extract (*MOE)

4.2.1Optimum dose of *Moringa oleifera* seed Extract (MOE)

Standard jar tests were conducted employing a test Fluoride solution of 5mg/L and coagulant doses ranging from 100mg/L to 2000mg/L. As the dose was increased progressively from 100 to 2000mg/l, removal percentage also increased from around 8% at 300mg/l of MOE to 87% at 1000mg/l and subsequent increase in dosage has not resulted in any increase in Fluoride removal. The results are presented in Figure 7. The plot of Fluoride removal % versus dose of MOE exhibited a pattern of destabilization, as the coagulant dose was progressively increased and fairly remained constant even on further addition of the coagulant, which suggests that the coagulation is of chemical nature due to formation of chemical complexes, between the Fluoride ions and the long chained polymers present in *Moringa oleifera*.

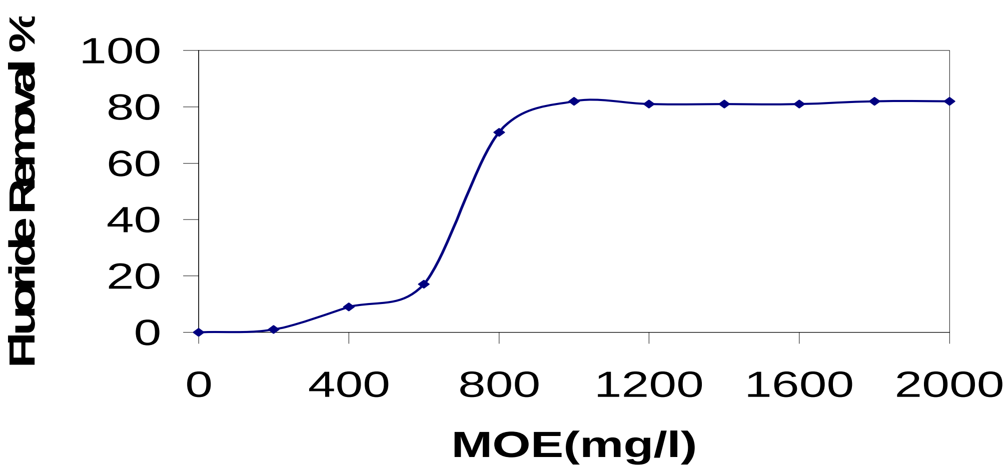

Figure 7. Effect of coagulant dose on Fluoride removal by *Moringa oleifera*.

4.2.2 Influence of pH on coagulative removal by MOE

Removal of Fluoride by MOE increased from 75% to 89% as pH was increased from 3 to 6. From pH 6 to 12 the Fluoride removal decreased from 89% to 77%. It may be observed that percentage removal of Fluoride is optimum at pH of 6.0 as in figure:8

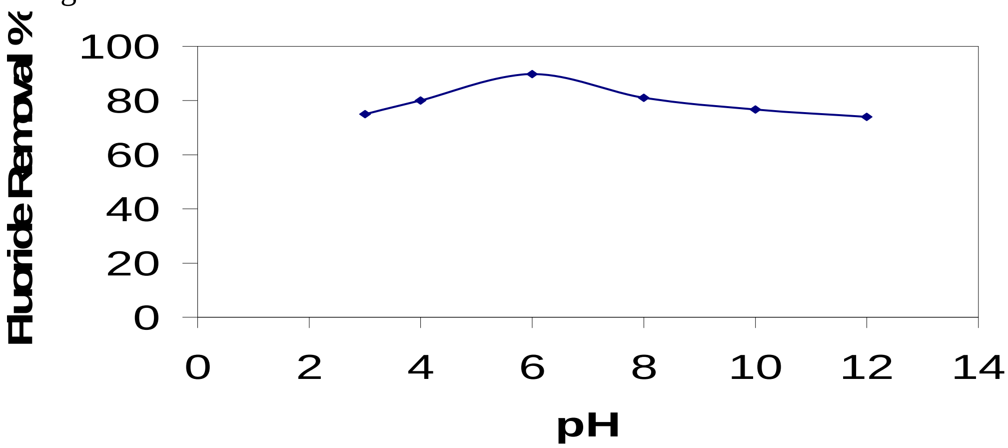

Figure 8. Effect of pH on coagulative removal of Fluoride by *Moringa oleifera*.

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4.2.3 Removal of Fluoride at optimum pH by MOE

Standard jar tests were conducted at a test Fluoride solution pH of 6.0±0.1 employing coagulant dose ranging from 100 mg/L to 2000 mg/L; percentage removal of Fluoride slightly increased by 4% due to favorable pH conditions and the results are presented in Figure 9.

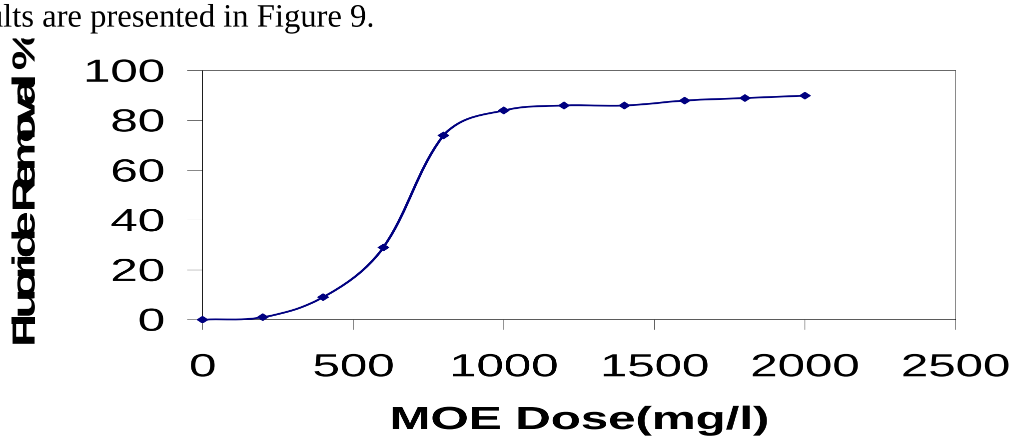

Figure.9 Removal of Fluoride by *Moringa oleifera* Extract at optimum pH

4.3 Removal of Fluoride by Manganese sulphate

4.3.1 Optimum dose of Manganese sulphate

As the dose of manganese sulphate was increased progressively in stages from 100 to 2000mg/L, percentage removal also increased yielding an optimum removal of 88% and the results are presented in Figure10. According to Srimurali [10], $MnSO_4$ was effective in removing colour of several types of dyes and colour removal was greater than 90 % for almost all the types of dyes that he investigated. $MnCl_2$ too exhibited almost the same percentage of removal of 90% with the coagulant dose being 500mg/l

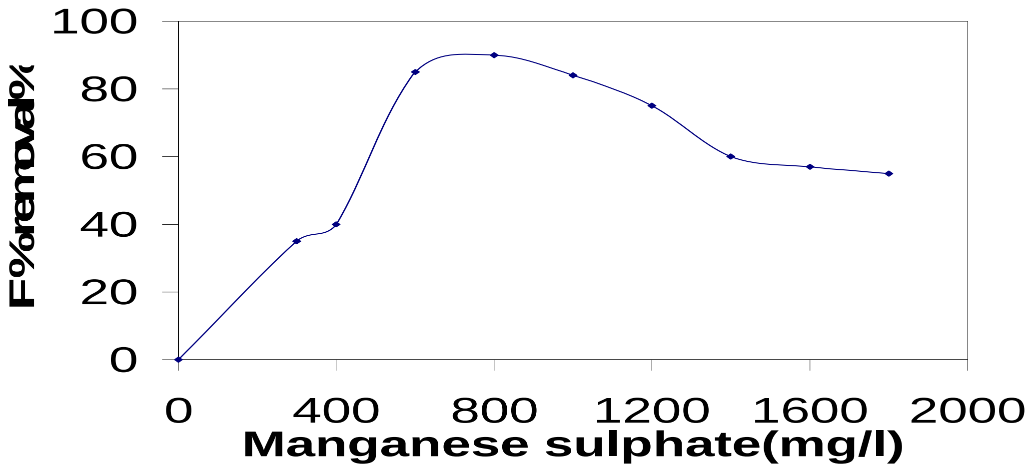

Figure.10 Effect of coagulant dose on Fluoride removal by Manganese sulphate

4.3.2 Influence of pH on coagulative removal of Fluoride by Manganese sulphate

To assess the influence of pH on coagulative removal by Manganese sulphate, standard jar tests were conducted by varying initial pH of the test Fluoride solution in the range of 3 to 12 and the results are presented in Figure 11. Removal of Fluoride by Manganese sulphate increased continuously as pH was increased from 3 to 6 from 60% to 88%. Beyond pH 6 Fluoride removals decreased from 88% to 68% at pH of 12.0. It may be observed that percentage removal of Fluoride is optimum at a pH of 6.0.

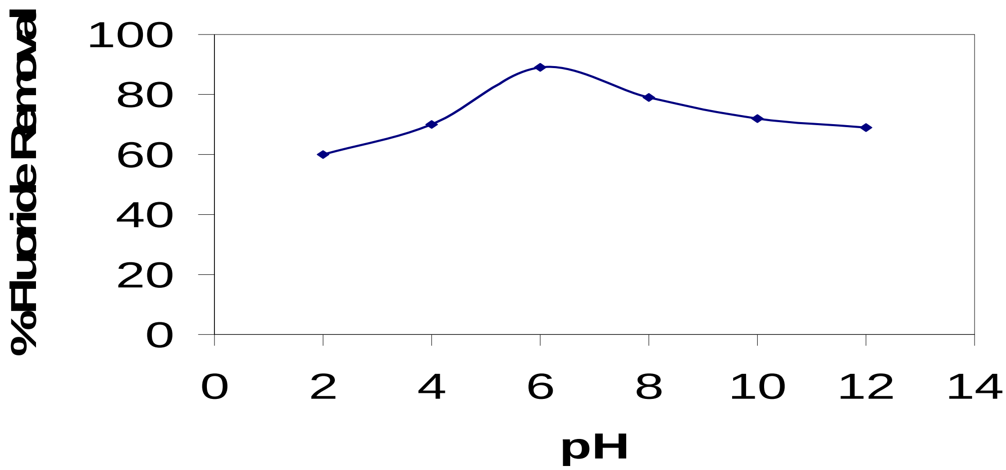

Figure 11. Effect of pH on coagulative removal of Fluoride by Manganese sulphate

4.3.3 Removal of Fluoride at optimum pH by Manganese sulphate

Standard jar tests were conducted at a test Fluoride solution pH of 6.0$\pm$ 0.1 employing coagulant dose ranging from 100 mg/L to 2000 mg/L and the percentage removal of Fluoride slightly increased by 5% at a coagulant dose of 750mg/l, due to favorable pH and the results are presented in Figure.12

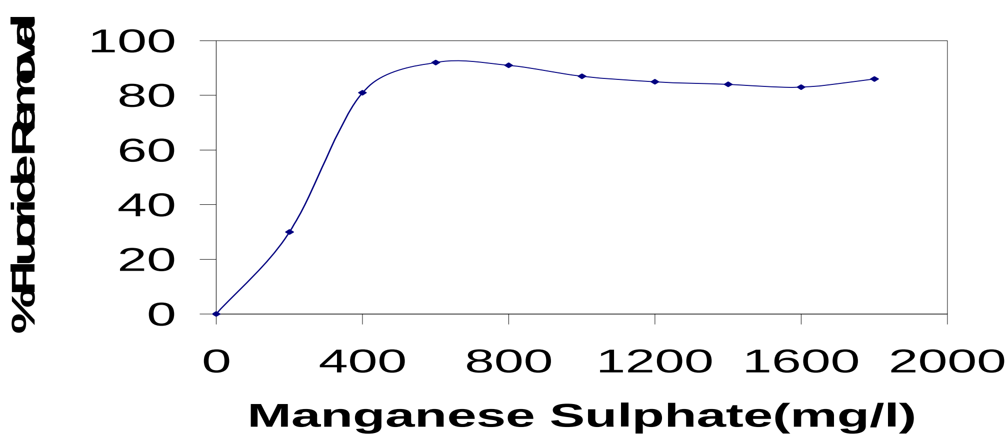

Figure.12 Effect of Manganese sulphate dose on Fluoride removal at optimum pH

4.4 Removal of Fluoride by Manganese chloride

4.4.1 Optimum dose of Manganese chloride

Standard jar tests were conducted employing a test Fluoride solution of 5mg/L and Manganese chloride doses ranging from 100mg/L to 2000mg/L. As the dose of Manganese chloride was increased progressively in stages from 100 to

2000mg/L, removal also increased reaching a maximum removal of 90% and the results are presented in Figure.13

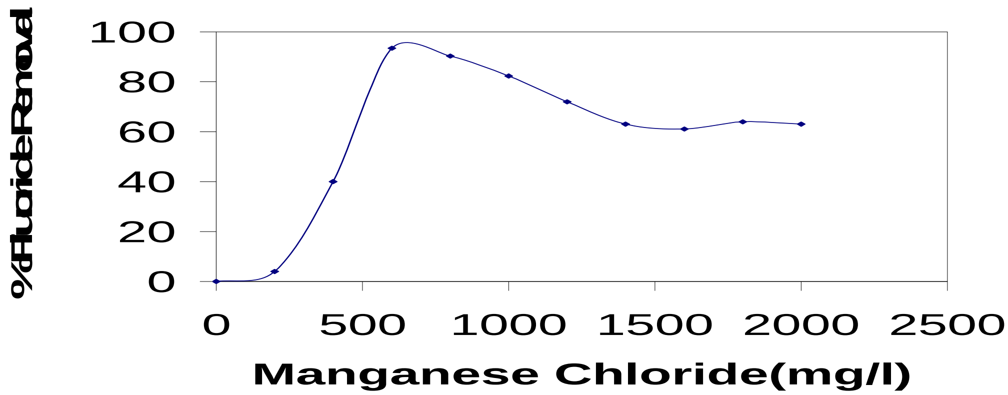

Figure.13 Effect of coagulant dose on Fluoride removal by Manganese chloride

4.4.2 Influence of pH on coagulative removal of Fluoride by Manganese chloride

To assess the influence of pH on coagulative removal of by Manganese chloride standard jar tests were conducted by varying initial pH of the test Fluoride solution in the range of 3 to 12 and the results are presented in Figure 14. Removal of Fluoride by Manganese chloride increased as pH was increased from 3 to 4 from 87% to 91%. Beyond pH 4 and upto 12 Fluoride removals decreased from 91% to 77%. It may be observed that percentage removal of Fluoride is optimum at a pH of 4.0.

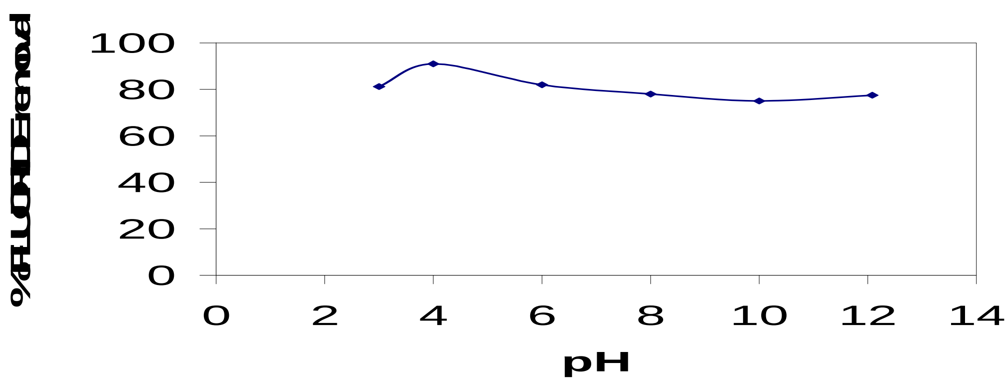

Figure.14 Effect of pH on coagulative removal of Fluoride by Manganese chloride

4.4.3 Removal of Fluoride at optimum pH by Manganese chloride

Standard jar tests were conducted at a test Fluoride solution pH of 4.0$\pm$ 0.1 employing coagulant dose ranging from 100 mg/L to 2000 mg/L the percentage removal of Fluoride slightly increased by 2% at the same optimum coagulant dose of 500mg/l, due to favorable pH and the results are presented in Figure.15

The optimum dose required for Fluoride removal remained the same whereas there was an increase of 2% removal at pH 4.0

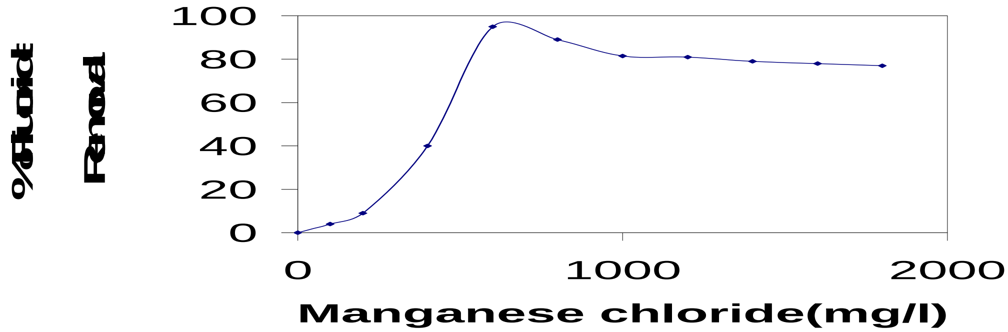

Figure.15: Effect of Manganese chloride dose on Fluoride removal at optimum pH

5.0 CONCLUSION

The experimental investigations clearly suggest that abundantly available and low-cost materials like Rice Husk, seed extracts of Moringa Oleifera (Drum stick) and chemicals like Manganese Sulphate and Manganese Chloride are effective in removing Fluoride from water to acceptable levels. Equilibrium isothermal sorption experiments suggested that sorbent dosages of 6g/l of rice husk accomplished a removal of 83% of Fluoride. The time to reach equilibrium was observed to be 3 hours. pH does not have any significant impact in the range of 3-10, where as pH of more than 10 resulted in a steep decrease in Fluoride removal. Manganese Sulphate, Manganese Chloride exhibited good percentage removal of Fluoride. Acid extract of natural Polyelectrolyte Moringa *Oleifera* seed is very effective as a coagulant for removal of Fluoride. A dose of 1000 mg/l removed 88% of Fluoride.

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