Effect of Simultaneous and Non-Simultaneous Mixing of Alum & Lime on Fluoride Removal Efficiency of Existing Nalgonda Technique

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Abstract: Drinking Water is the main source of fluoride intake in human beings. Fluoride intake can cause many health problems in humans if its consumption exceeds the maximum permissible limit of 1.5 mg/L as prescribed by WHO and BIS. Excessive Fluoride intake causes dental and skeletal fluorosis. It causes dental caries formation in children of growing age if its concentration in drinking water is less than 1 mg/L. In the present study, real fluoride contaminated groundwater site was identified and samples were collected from Karahari village of district Mathura, Uttar Pradesh, India. The water sample was analyzed for pH, fluoride, Potassium, Arsenic, Nitrate, Iron, Chloride, sulphate, hardness, Sodium, alkalinity and calcium. Fluoride concentration of 5.11 mg/L was found in the groundwater sample, which is more than the upper limit (1.5 mg/L) of Indian drinking water standards (IS10500:2012). Rest of the parameters were found to be within the permissible limit of Indian drinking water standards (IS10500:2012). Fluoride contaminated groundwater was treated using Nalgonda Technique after optimizing the alum and lime doses. Effect of simultaneous and non-simultaneous mixing of alum and lime was also studied for synthetic fluoride water and groundwater. More fluoride removal was obtained when alum and lime were mixed non-simultaneously in groundwater as well as in synthetic fluoride water. Around 10 % more fluoride removal was obtained from synthetic fluoride water in the case of non-simultaneous mixing of alum and lime at randomly selected dose combinations of alum and lime. In the case of groundwater around 6.66 %, more fluoride removal was obtained when alum and lime were mixed non-simultaneously at optimized doses of alum. It was concluded that non-simultaneous mixing of alum and lime should be practiced to achieve more efficiency in Nalgonda Technique for removal of fluoride from contaminated water.

Keywords- Fluoride, Nalgonda Technique, Treatment, Groundwater, Chemical dose optimization.

I. INTRODUCTION

Fluoride is the ionic form of the elemental fluorine. Due to more electronegativity fluorine is not found in its elemental state in the natural environment. It is found in nature in the form of fluorides. It forms mineral complexes with cations. Ionic radius and sizes of fluoride and hydroxyl ions are same [1]. Fluoride can easily replace hydroxyl ion present in the teeth and bones of living creatures as a subunit [2]. The concentration of fluoride in the underground water varies place to place which depends upon physical, chemical, geological characteristics of the aquifer, depth of the well, actions of chemical elements, temperature, porosity, the acidity of rocks and soil [3].

Fluoride is very helpful in preventing, dental carries if taken in optimal amount but it is not possible to get optimal amount daily because there is a variation in individual nutritional status and this influences the rate of absorption of fluoride by the body. If a diet is having less amount of calcium then there are more chances of fluoride retained in the body [3]. Around 90 % rural population of India is using the groundwater for drinking and domestic purposes. In India, 184 districts of 19 states have fluoride concentration more than the limit prescribed by the World Health Organization [4].

Precipitation, Adsorption, Membrane filtration and Ion exchange methods are used to treat fluoride contaminated water. Nalgonda technique is the example of precipitation based method of fluoride treatment. Both cation and anion

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exchange resins like Amberlite XAD-4™ , Amberlite IR-120, Polyanion (NCL), Ceralite IRA 400, Indion FR 10 have been used for the removal of fluoride[5], [6],[7],[8]. Many adsorbents like activated alumina, calcined clay, bone charcoal etc. are used to treat fluoride contaminated waters[1]. Membrane based techniques like Electrodialysis, reverse osmosis and nano filtration are used to treat fluoride contaminated water.

In developing countries like India, fluoride contaminated groundwater should be treated using a suitable, cost-effective and easily operable method. Nalgonda technique is one of the most practiced methods of fluoride treatment in India, which removes fluoride by precipitation technique. Nalgonda technique is being used at both communities as well as household level in India, Denmark, and some African countries. Buckets or drum defluoridation systems have been developed for the domestic level. Fill and draw type defluoridation systems have also been reported at community levels[9]. This technique is having less cost and good efficiency. The Nalgonda Technique was developed in India by the National Environmental Engineering Research Institute (NEERI). In Nalgonda technique alum and lime is added to fluoride-rich water to get water with low fluoride content. Doses of Alum and lime are optimized for ensuring the fluoride removal from the water. Main focus of the present study is to know the effect of simultaneous and non-simultaneous mixing of alum and lime on fluoride removal efficiency of Nalgonda technique.

1.1 Nalgonda Technique: Treatment Mechanism

Nalgonda Technique treats water in two steps. In the first step, lime is added to the water which causes precipitation after that alum is added to water in the second step to cause coagulation. Two reactions occur when alum is added to the water. In the first reaction, Alum reacts with some of the alkalinity to produce insoluble aluminium hydroxide.

In second reaction alum reacts with the fluoride ions present in the water. Best fluoride removal is accomplished at a pH level ranging from 5.5 to 7.5[10]. Lime addition leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water up to 12[11]. The reaction of the same is explained in equation 1 as follows.

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \qquad (1)$$

As lime leaves a residual fluoride of 8 mg/L, it is used only in conjunction with alum treatment to ensure the proper fluoride removal[12]. After the dissolution of Alum into the raw water, the acidity of solution gets increased (Eq.3). Simultaneous addition of lime is needed to ensure neutral pH in the treated water (Eq.4) and complete precipitation of aluminium(Eq.3). Aluminium hydroxide flocs are produced in the coagulation process. These flocs are gathered into larger sized settable flocs in the flocculation process. During the flocculation process, fluoride and microparticles are removed by electrostatic attachment to the flocs (Eq.5). After this, the mixture is allowed to settle. The supernatant is stored separately as treated water. Filtration is also applied to avoid sludge particles in the treated water. Equation 2, 3, 4 and 5 explain the chemical reactions take place during the whole process[1].

Alum Dissolution:

$$Al_2(SO_4)_3 18H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 18H_2O \qquad (2)$$

Aluminium Precipitation:

$$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+ \qquad (3)$$

pH Adjustment:

$$6Ca(OH)_2 + 12H^+ \rightarrow 6Ca^{2+} + 12H_2O \qquad (4)$$

Co-precipitation (non-stoichiometric, unidentified product):

$$F^- + Al(OH)_3 \rightarrow Al - F \text{ (Complex) + Unidentified Product} \qquad (5)$$

1.2 Summary of the literature and Objective of the Study

Madhukar, et al. [13] have been reported that the process is initiated by the addition of lime to the raw water followed by rapid mixing and alum is added during slow mixing. Potgeiter [10] concluded that the process starts with the addition of lime as the first step. Alum is added in the second step to cause coagulation. But according to Fawell [1], the simultaneous addition of lime is needed to ensure neutral pH in the treated water. Dahi [9] has reported that initial mixing time and intensity, the slow stirring time and intensity, the shape of the container and if any of the two chemicals added first are of minor importance for the removal as compared to the dose of alum at the right pH. It means a proper sequence of addition of both chemicals is not the same among the authors or it is of minor importance. To check the effect of the sequence of addition of both chemicals has any effect on fluoride removal, the present study was aimed to:

1) Collect fluoride contaminated groundwater from the contaminated site
2) Analyze the groundwater sample
3) Optimize Alum and lime doses for treating the groundwater using Nalgonda Technique
4) Study the effect of simultaneous and non-simultaneous mixing of lime and Alum on the fluoride removal efficiency

II. MATERIALS AND METHODS

2.1 Reagents and Instruments for Fluoride Detection

The concentration of fluoride during the whole study was determined by using the SPADNS method [14]. Zirconyle

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acid reagent was prepared by dissolving Zirconyle Chloride Octahydrate, $ZrOCl_2.8H_2O$ in about 25 ml Milli Q water. After that 350 ml concentrated HCl was added to it. Then this whole solution was diluted to 500 ml with Milli Q water. The SPADNS solution was prepared by dissolving 958 mg SPADNS in Milli Q water and diluting to 500 ml. Spectrophotometer absorbance readings were taken at wavelength 570 nm.

2.2 Sample Collection and Analysis

High concentration of fluoride in the Mathura district of Uttar Pradesh has been reported. Groundwater was collected in a polyethylene bottle from a handpump located in the village Karahari, Mathura, Uttar Pradesh. The sample was analyzed for pH, Fluoride, Arsenic, Nitrate, Iron, Chloride, Sulphate, Hardness, Sodium, Potassium, Alkalinity, and Calcium.

2.3 Nalgonda Technique: Chemicals, Apparatus, and Process Parameters

In experiments were carried out using the standard laboratory jar test apparatus with six stirrers. The stirrers were rotated at 145 revolutions per minute (rpm) for 1 minute during the rapid mixing. Slow mixing was done at 34 revolutions per minute (rpm) for 15 minutes. Aluminium Potassium Sulphate ($AlK(SO_4)_2.12H_2O$) salt with assay 99-102 % was used as alum source in the whole study. Calcium oxide powder (CaO) with assay 95 % was used as a lime source.

2.3.1 Fluoride Removal from Synthetic Fluoride Water

Before going for alum and lime dose optimization for groundwater, the difference in the removal of fluoride from synthetic fluoride solution was checked for both simultaneously & non-simultaneously added lime and alum. The constant lime dose of 100 mg/L was provided in six beakers having one-liter synthetic fluoride solution in each with an initial fluoride concentration of 5.54 mg/L. Out of six beakers, alum dose of 600, 800 and 1000 mg/L was provided to three beakers and rapid mixing was done for one minute at 145 rpm in all beakers. Figure 2 shows the flow of the treatment process when alum and lime are mixed non-simultaneously.

In remaining three beakers alum dose of 600,800 and 1000 mg/L was provided during slow mixing. Slow mixing was done for 15 minutes at 34 rpm and flocs were allowed to settle for 30 minutes. Figure 1 shows the flow of the treatment process when alum and lime are mixed simultaneously. The supernatant was sampled from each beaker and filtered through grade 1 Whatman filter paper (Whatman 1001-125). Analysis of all samples was done for residual fluoride concentration after filtration.

2.3.2 Fluoride Removal from Groundwater

Fluoride concentration in the groundwater sample was found to be 5.11 mg/L which is more than the Indian drinking water standards upper limit of 1.5 mg/L. Fluoride concentration more than the 1.5 mg/L has been reported in Mathura district of Uttar Pradesh[4], [15].Table1 shows the characteristics of the groundwater sample. Varied alum doses from 125 mg/L to 1500 mg/L were applied to different beakers of jar test apparatus having one-liter fluoride contaminated groundwater in each. The water was allowed to stand for 30 minutes and the supernatant was sampled from each beaker. Residual fluoride was checked in each sample after filtering through grade 1 Whatman filter paper. Optimum alum dose with maximum fluoride removal was selected. Variation in lime dose was done from 25 mg/L to 125 mg/L at a fixed (Optimum) alum dose & effect of simultaneous and non-simultaneous mixing of alum and lime was also checked along with lime dose optimization.

In one set of experiment, alum doses were applied during rapid mixing along with lime doses. In the second set of experiment, alum doses were applied during slow mixing. After that solution of each beaker was allowed to stand for 30 minutes. The supernatant of each beaker was filtered by grade 1 Whatman filter paper & analyzed for residual fluoride concentration. Best combination of lime and alum with significant removal of fluoride was selected.

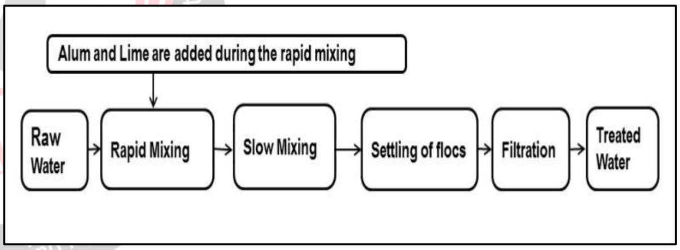

Figure 1: Flow diagram of the treatment process when alum and lime are mixed simultaneously.

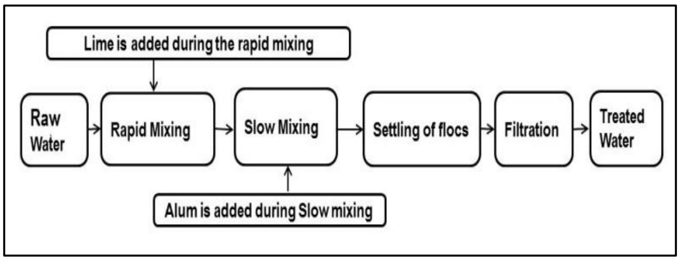

Figure 2: Flow diagram of the treatment process when alum and lime are mixed Non-simultaneously.

S.No.	Parameter	Concentration
1.	Fluoride (mg/L)	5.11
2.	Chloride (mg/L)	211
3.	Nitrate (mg/L)	41.08
4.	Sodium (mg/L)	285.12
5.	Sulphate (mg/L)	269
6.	pH	7.90

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7.	Arsenic (ppb)	4.44
8.	Hardness(mg/L as $CaCO_3$)	278
9.	Iron (mg/L)	0.24
10.	Calcium (mg/L)	71.20
11.	Potassium (mg/L)	16.11
12.	Alkalinity (mg/L as $CaCO_3$)	387

Table 1: Characteristics of the groundwater.

III. RESULT AND DISCUSSION

3.1 Fluoride Removal from Synthetic Fluoride Water

During the study, it was observed that the removal of fluoride was more when alum and lime were added non-simultaneously. Figure 3 shows the effect of the simultaneous & non-simultaneous addition of lime and alum on fluoride removal from the synthetic fluoride water. Residual fluoride concentration was 3.31, 3.48 & 3.98 mg/L for 600, 800, 1000 mg/L dose of alum, respectively, when alum and lime were mixed simultaneously. For non-simultaneous addition of lime and alum residual fluoride concentration was 2.80, 3 & 3.31 mg/L for same doses of alum. Thus around 10 % more removal of fluoride was achieved in the case of non-simultaneous mixing of alum and lime. Percentage fluoride removal analysis data is given in table 2. More removal of fluoride in the case of non-simultaneous mixing might be due to the occurrence of both reactions of fluoride removal as per the equation (1) and (5). Less removal in the case of simultaneous mixing of alum and lime might be due to the occurrence of only one reaction of fluoride removal as per the equation (5).

Alum Dose (mg/L)	Percentage Removal (%)			
	Simultaneous Mixing	Non-Simultaneous Mixing	Difference	Average
600	40.25	49.46	9.21	9.99 ≈ 10
800	37.18	45.85	8.67	
1000	28.16	40.25	12.09	

Table 2: Percentage fluoride removal analysis data for simultaneous and non- simultaneous mixing of alum and lime.

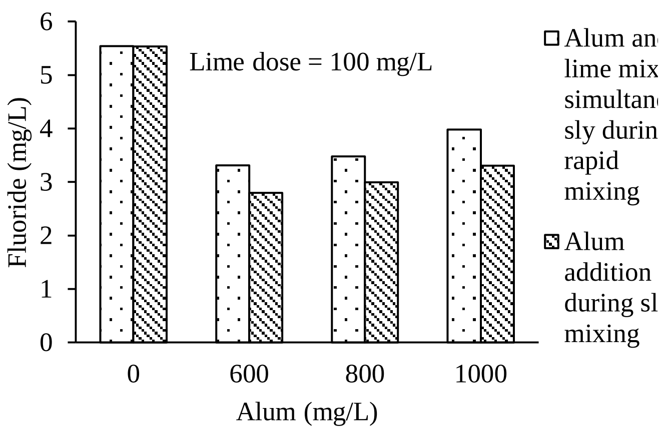

Figure 3: Effect of simultaneous & nonsimultaneous addition of alum and lime on fluoride removal.

3.2 Alum Dose Optimization for Removing Fluoride from Groundwater

Figure 4 shows the fluoride removal and change in pH at different alum doses. It was observed that up to 1000 mg/L dose of alum fluoride removal was increased and started decreasing on further increase in the dose of alum. With 5.11 mg/L of initial fluoride concentration, 1.95 mg/L of minimum residual fluoride was observed when treated with 1000 mg/L dose of alum. So, 1000 mg/L dose of alum was selected as an optimum dose for all further studies. A decrease in pH level of the solution was observed with the increase in dose of alum. The initial pH level of 7.90 was observed to be decreased up to 4.54 at 1500 mg/L. A pH level of 5.98 was observed at 1000 mg/L dose of alum. Fawell [1] has also reported that after the dissolution of alum into raw water acidity of water gets increased as per the equation 3.

3.2.1 Lime Dose Optimization for Removing Fluoride from Groundwater: Simultaneous Mixing of Alum & Lime

Minimum residual fluoride concentration of 1.95 mg/L was found at 50 mg/L dose of lime and became constant on the further increment of lime dose. Graphical representation of the whole data is given in figure 5. It was also observed that pH of the solution was initially decreased to 5.75 from an initial pH of 7.90 at 25 mg/L lime dose. After that, there was an increase in pH with an increase in dose of lime. Maximum removal was observed at pH 5.89.

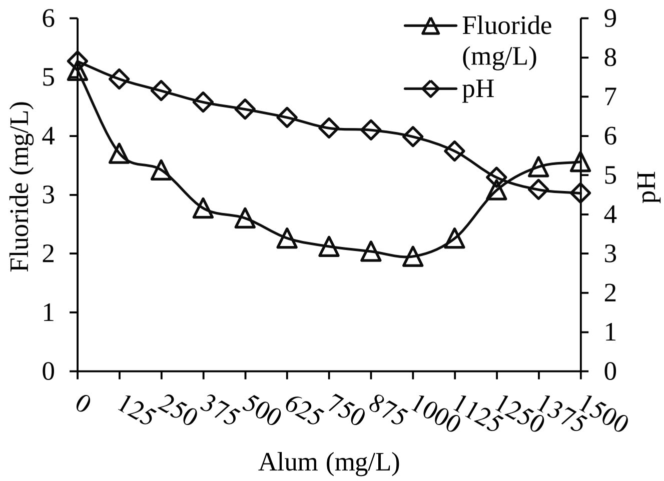

Figure 4: Alum dose optimization along with change in pH.

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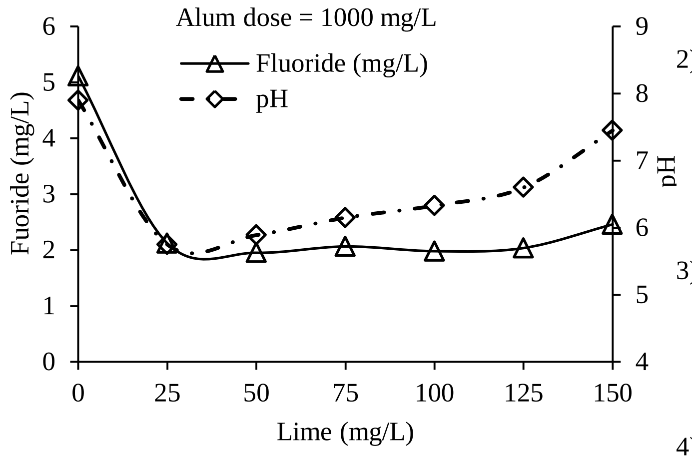

Figure 5: Lime dose optimization when alum & lime were mixed simultaneously.

3.2.2 Lime Dose Optimization for Removing Fluoride from Groundwater: Non-Simultaneous Mixing of Lime and Alum

Lime dose optimization data for non-simultaneous addition of alum and lime is given in figure 6. More fluoride removal from the groundwater was obtained in case of non-simultaneous mixing of alum and lime as compared to simultaneous mixing of alum and lime. At a lime dose of 25 mg/L, fluoride was removed up to 1.78 mg/L from an initial concentration of 5.11 mg/L. Fluoride removal was found to be almost constant up to a lime dose of 125 mg/L. At lime doses of 100 and 125 mg/L maximum removal was obtained with a residual fluoride concentration of 1.61 mg/L which is very near to the upper drinking water standards limit of India. Residual pH of 6.55 was obtained at a lime dose of 125 mg/L which is within the range of pH (6.5-8.5) prescribed by Indian standards for drinking water (IS10500:2012). So, 125 mg/L dose of lime was selected as an optimum lime dose. At optimized doses of alum and lime around 68.5 % removal of fluoride was achieved.

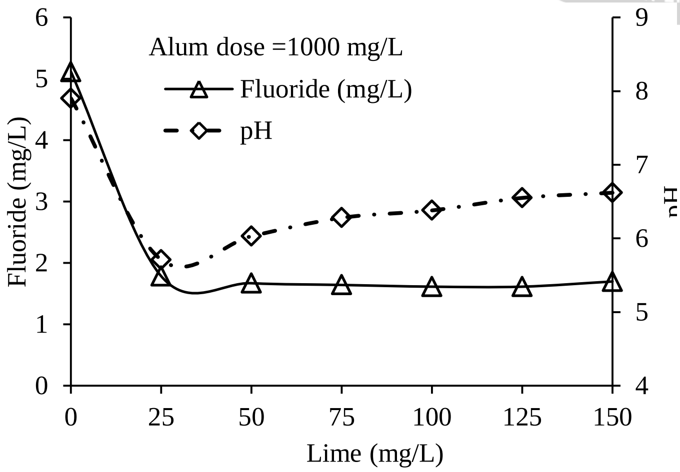

Figure 6: Lime dose optimization when lime and alum were mixed non-simultaneously.

IV. CONCLUSION

1) Fluoride concentration in the groundwater sample was found to be 5.11 mg/L which is more than the Indian drinking water standards limit of 1.5 mg/L. It means the groundwater is contaminated with fluoride.
2) Fluoride removal in the case of synthetic fluoride solution is more when lime and alum are mixed non-simultaneously at randomly selected dose combinations of alum and lime. Around 10 % more fluoride removal from synthetic fluoride water was obtained in the case of non-simultaneous mixing of alum and lime.
3) Optimized doses of lime and alum for the groundwater collected from a hand pump of Karahari village, Mathura, Uttar Pradesh are 125 and 1000 mg/L respectively provided that lime and alum have mixed non-simultaneously.
4) At optimized dose of alum and lime residual pH and fluoride concentration of the groundwater was found to be 6.55 and 1.61 mg/L respectively.
5) Removal of fluoride from the groundwater was also more in the case of non-simultaneous mixing of alum and lime at optimized doses of alum and lime. Percentage removal of fluoride from the groundwater is 68.5 % and 61.84 % in the case of non-simultaneous and simultaneous mixing of alum and lime respectively. Thus around 6.66 % more removal was obtained in the case of non-simultaneous mixing of alum and lime.

V. RECOMMENDATIONS

1) As the groundwater used in the present study is contaminated with fluoride therefore it is recommended to treat this water properly using a suitable technique before the consumption.
2) For achieving higher efficiency in the existing Nalgonda Technique it is recommended to mix alum and lime non-simultaneously i.e. addition of lime during rapid mixing and addition of alum during slow mixing (As per figure number 2).

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