SORPTION ISOTHERMS OF FLUORIDE ON FLOCCULATED ALUMINA

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SUMMARY: A new model for the design of alum dosage in the flocculation-sedimentation process for defluoridation of water is developed. It is based on the finding that correlation between the fluoride residual in the water and the concentration of the uptaken fluoride in the flocculated alum follows a Freundlich isotherm for identical residual pH in the treated water. The sorption capacity constant α is estimated to be 6.5 $mg^{1-1/\beta} \cdot L^{1/\beta} \cdot g^{-1}$, and the sorption intensity constant β is estimated to be 1.4, valid for optimum pH in the treated water. This was found to be between 6.2 and 7.0. Deviation from this range may cause a significant decrease in the removal efficiency of the added alum. It is recommended that the addition of lime should no longer be 5% of the alum dosage, as given in the Indian Guidelines, rather adjusted in order to reach the optimum pH. In Tanzania waters this was found to account 20-50 % of the alum dosage.

Key words: Alumina, fluoride, sorption isotherms, Nalgonda technique, lime, defluoridation, pH-optimum.

INTRODUCTION

Defluoridation of water is mainly based on two categories of techniques. The first is the flocculation-sedimentation and the second is the filterbed sorption. Aluminum components are well known to be applicable in both categories, e.g. the use of alum in flocculation-sedimentation and the use of activated alumina in column sorption. Especially the use of alum, i.e. aluminum sulfate or potassium aluminum sulfate has been tested for defluoridation of water in many countries.

Since its discovery by Boruff in 1934[1], the defluoridation by means of alum has been studied and developed by many workers. Cheap and simple as it is, the alum process has been studied mainly for use in developing countries. The work carried out by the National Environmental Engineering Research Institute, NEERI, in India has been most significant and resulted in development of the technique at a small water works in the Nalgonda town in the Southern part of the country. Furthermore, detailed testing and dosage design criteria were developed.[2] The mechanisms of removal are not yet completely understood. While the activated alumina defluoridation has been understood as a sorption process, the Nalgonda technique has mainly been understood as a "co-precipitation". This is probably due to lack of a simple stoichiometric correlation between the added alum and the obtained fluoride removal.

The purpose of this study is to elaborate on the significance of pH on optimization of the dosage of alum and lime. Furthermore to develop a scientific tool for estimating of the required dosage of alum, as a function of the contents of fluoride in the raw water and the required residual concentration in the treated water.

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MATERIALS AND METHODS

Two types of experiments were carried out using a jar test apparatus (Phipps & Birds Stirrer 7790-402), as 6 batches in parallel. Each batch consisted of 1-L plastic beakers containing 1 L solutions of sodium fluoride, analytical grade, in distilled water at different given initial concentrations and pH-buffering. The temperatures were 20 ± 1°C.

Dosage Determination Experiments. In the first type of experiments, pH was allowed to vary as a function of the dosage of alum and lime. Alum, technical grade normally used in water works, was added together with lime as powder. The chemicals were added at time nil to alle jars in parallel. The beakers were mixed vigorously using 100 RPM paddle stirring for ½ minute. Then slow mixing, 25 RPM, was carried out for 10 minutes. Hereafter 1 hour of settling before measurement of pH and fluoride concentrations. Alle experiments and measurements were carried out in 2-4 replicates. The Nil dosage was used as a control.

pH-controlled Experiments: In the other type of experiments pH = 6.8 was controlled by pre-addition of 0.025M buffer of KH_2PO_4 and Na_2HPO_4, both pro analysis. Each experiment was carried out in 2-4 replicates.

Fluoride and pH Measurements: The concentration of fluoride and pH in the water were both measured and monitored continuously using a Radiometer F1052 fluoride electrode and Metrohm Ag/AgCl reference electrode with sleeve type diaphragm connected to a Metrohm 691 pH-meter. Tisab[3] was added to 5 mL samples taken for fluoride measurements according to Standard Methods.[4]
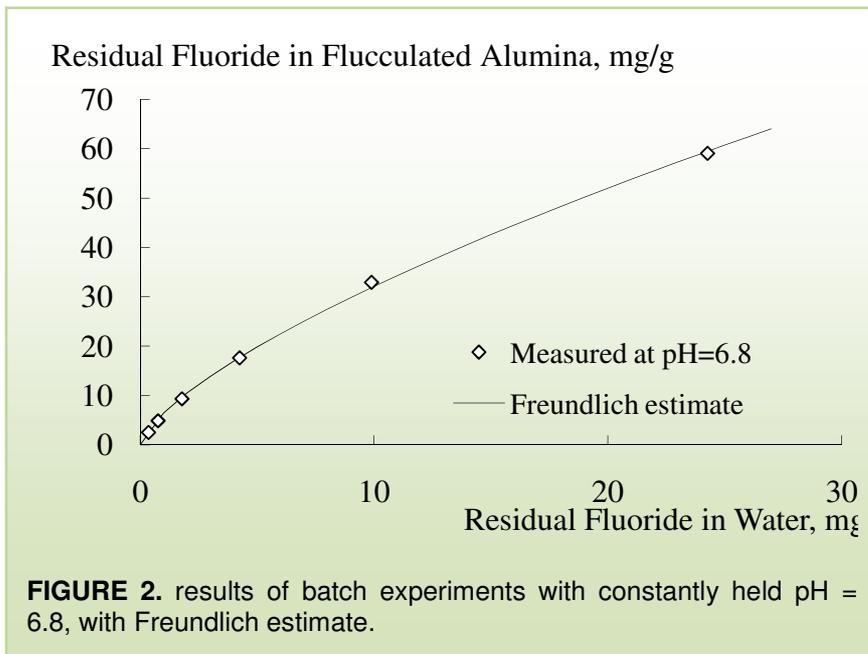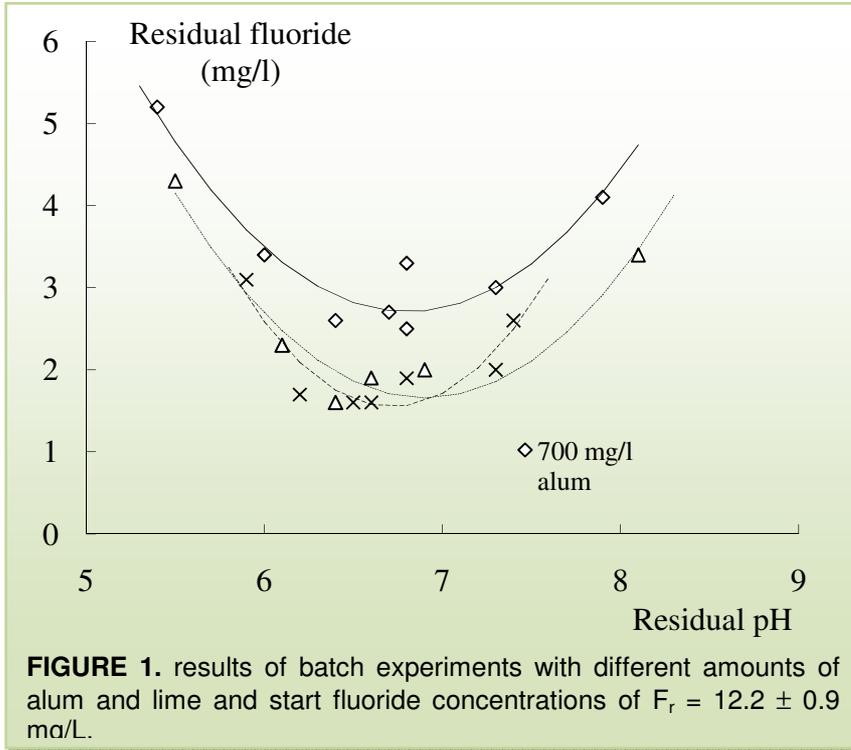
RESULTS

By adding alum to water containing 12.2 ± 0.9 mg F/L at three different levels, different removal efficiencies are obtained. Figure 1 illustrates the obtained residual concentration as a function of residual pH. The different pHs are obtained because of different additions of lime, between 75 and 350 mg/L. It is seen that fluoride removal efficiency varies between 54 and 79 % for the same dosage level, 700 mg/L alum. Similar figures are obtained for the other dosage levels applied. Clearly, the removal has an optimum within the range pH 6.2 to 7.0. This phenomena is well-known for removal of silt by the same method and has also been reported for fluoride by Lagaude *et al*.[5]

Designating the amount of added alum as A (in g), the volume of treated water as V (in L), and the concentration of fluoride in the raw and treated water as F_r and F_t (in mg/L), the concentration of removed fluoride in the flocculated aluminum f (measured as mg F/g added alum) may be calculated as

$$f = \frac{(F_r - F_t) \cdot V}{A}$$

When this fluoride density in the "flocculated alum" is correlated to the residual concentration of fluoride in the water, a very scattered picture shows up, as long as pH is not controlled. However, when the same correlation is determined for a given residual pH, the correlation turns out to be a Freundlich type, figure 2.

FIGURE 1. results of batch experiments with different amounts of alum and lime and start fluoride concentrations of F_r = 12.2 ± 0.9 mg/L.

FIGURE 2. results of batch experiments with constantly held pH = 6.8, with Freundlich estimate.

$$A = \frac{(F_r - F_t) \cdot V}{\alpha \cdot F_t^{1/\beta}}$$

Where:

α is the sorption capacity constant, the unit being $mg^{1-1/\beta} \cdot L^{1/\beta} \cdot g^{-1}$

β is sorption intensity constant, dimensionless.

The results showed that, for residual pH = 6.8 and residual fluoride concentration F_t between 0.35 and 24 mg/L:

α = 6.5 $mg^{1-1/\beta} \cdot L^{1/\beta} \cdot g^{-1}$

β = 1.4

The results of this and other studies of ours show that the amount of lime required to obtain optimum pH may vary as much as 20-50 % of the added alum. Thus it has not been possible, if optimum pH are to be achieved, to develop valid guidelines about how much lime should be added. The amount of lime seems to be dependent on several factors, including the alkalinity of the water, the added amount of alum, the removed fluoride, and above all on the quality of the used lime.

DISCUSSION

Figure 1 confirms that larger amounts of alum can be used without gaining correspondingly more efficient removal of fluoride. Furthermore it is seen that high dosage of alum, i.e. more than 1,000 mg/L is required in order to treat water having fluoride contents about 10 mg/L, even when a residual concentration of 1.5 mg/L is accepted. Such high concentration of alum would result in too high concentrations of sulfate in the treated water. All sulfate, about 43% of the added alum, would reside in the water, along with waters original content of sulfate. Water containing more than 250 mg/L sulfate is taken by some consumer as a little bit "salty", and 500 mg/L sulfate may cause laxative effect among the consumers, first and foremost the children[6]. Thus there are good reasons to rationalize the design of defluoridation by alum. On one hand it may be difficult to obtain sufficient removal of fluoride, on the other hand it may be difficult to avoid impairing the water quality with respect to sulfate.

In the guidelines for defluoridation published by NEERI in 1987[7], later confirmed in guidelines of 1993[8], the alum required to reduce the fluoride contents of a water from 10, 8, 6, 5, 4, 3 and 5 mg/L down to 1 mg/L are presented in a table form. The table includes selected contents of alkalinity of the raw water, between 125 and 1,000 mg $CaCO_3$/L. Unfortunately, the experiences gained in Tanzania and in Denmark have shown that the usability of these design guidelines has two serious limitations.

Firstly many water sources have fluoride/alkalinity characteristics outside the ranges presented in the NEERI table. In such a situation, as found in the Arusha region in East Africa, the NEERI guidelines are of less use.

Secondly, addition of lime, as recommended by NEERI to be 5 % of the added alum, have shown to result in pH-values in the treated water, which are significantly different from what is optimum for the fluoride removal. This study has shown that any addition of lime which may result in pH values different from 6.2 - 7.0 would reduce the effectiveness of the treatment. Furthermore it may be seen from figure 1 that the reduction of effectiveness may be quite significant even for 1 unit deviation from the optimum range.

On this background it may be considered as an advantage to use the Freundlich correlation for design purposes. However, the Freundlich formula does not include the dependency of the sorption constants on pH. Thus it may give the false impression, that the same constants can be used for any residual pH. Probably this could be solved by deriving another formula for the dependency of the sorption constants on pH. From practical point of view however, only optimum pHs are of interest.

The results of this study indicate that α, on the contrary to β, is dependent on pH. For engineering design, β may be assumed to be constant, 1.4. This simplification may be utilized to estimate an appropriate α for any given treatment conditions. In this way one could take into consideration locally determined variations in water quality and alum characteristics.

CONCLUSION

The removal of fluoride in the alum flocculation-sedimentation process is highly dependent on the residual pH of the water, the optimum is estimated to be obtained at pH = 6.2 - 7.0. The addition of lime should then be adjusted to obtain the optimum pH in the treated water. In such a case the residual fluoride concentration shows a Freundlich type sorption isotherm, which may be used in the process design for estimation of the required alum dosage.

ACKNOLEGMENTS

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