Reduction of Fluoride Concentration Applying Micro-Nano Bubble Pre-treatment Process

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Abstract

Fluoride concentration in water is very important from environmental and health aspect. Optimal fluoride content is below 1 ppm. Micro-nano bubble pretreatment was used in this study to observe the fluoride removal efficiency. After 2 hours of air bubble pre-treatment, $Ca(OH)_2$ was added until pH 10. And then several standard reagents like Poly Aluminum chloride, Aluminum Sulfate, F900 and two polymers namely A-polymer and A430P polymer were used in this study with raw and air bubble pre-treated wastewater. After the entire experiment, the fluoride removal efficiency from air bubble pretreated wastewater was higher than the raw wastewater. It was found that the combination of PAC 11% and A430P polymer with air bubble pre-treated wastewater seems to have a higher fluoride removal percentage than the other combinations(76.94%) and in case of COD removal, the combination of Alum and A430P polymer with air bubble pre-treated wastewater was observed to be the best(64.6%) while the removal percentage from the wastewater without pre-treatment is 71.43% for fluoride and 57.18% for COD.

Keywords : Micro-nano bubble, Fluoride, Pre-treatment, Industrial wastewater, Polymer

1. Introduction

Water is essential for all being. It is needed for the survival of human beings, animals, plants and environment. It is one of the major elements essential for sustenance of all forms of life in nature. Almost three fourth of the surface of the earth is water.

So it is very obvious that water is very easily accessible to all and that if contaminated, it has serious affects on all of us. Among many contaminants, fluoride in excess amount poses high risk to human health. Throughout many parts of the world, high concentrations of fluoride occurring naturally in groundwater and coal have caused widespread fluorosis - a serious bone disease - whether dental or skeletal, this disease is irreversible. Fluoride ions can be found from wastewaters derived from semiconductor, metal processing, fertilizers and gas manufacturing industries[1-4]. We purposely fluoridate a range of everyday products, notably toothpaste and drinking water, because for decades we have believed that fluoride in small doses has no adverse effects on health to offset its proven benefits in preventing dental decay. But more and more scientists are now seriously questioning the benefits of fluoride,

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even in small amounts[5]. Water is a major source of fluoride intake. The 1984 WHO guidelines suggested that in areas with a warm climate, the optimal fluoride concentration in drinking water should remain below 1 mg/L(1 ppm or part per million), while in cooler climates it could go up to 1.2 mg/L. There has been a growing concern over the toxic and adverse effects of fluoride on human health. Fluoride intake above the permitted amount may lead to several diseases like Alzheimer's, osteosarcoma(a rare form of bone cancer in young males), genetic mutations, hypothyroidism, infertility, early onset of puberty, kidney damage, gastrointestinal problems and so many others. The fluoridation guideline tells us that 1 ppm fluoride is normal to add in public water supply. But according to the Journal of the American Dental Association 1936 and 1944, "Fluoride at the 1 ppm concentration is as toxic as arsenic and lead and the use of drinking water containing as little as 1.2 to 3 ppm of fluoride will cause many diseases like cancer and fluorosis". Many People in the world are affected by fluorosis, especially in China, India, Pakistan and Thailand[7].

There are several methods for removing fluoride from water or wastewater such as chemical precipitation method[3,4,6-11,13], activated alumina, bone char, degreased or alkali treated bones, synthetic tricalcium phosphate, florex, activated carbon, lime, ion exchange resins, magnesia, serpentine, fly ash, electrochemical methods etc. The use of activated alumina in a continuous flow fluidized system is an economical efficient method for defluoridation[13]. Most of the carbons prepared from different carbonaceous sources showed fluoride removal capacity after alum impregnation. High fluoride removal capacities of various types of activated carbon have been reports[14]. The fluorides in waters containing Magnesium when treated with lime are adsorbed on Magnesium Hydroxide flocks enabling fluoride removal[15-17]. Electro coagulation process with aluminum bipolar electrodes was used for defluoridation process. The influence of parameters such as inter-electrode distance, fluoride concen- tration, temperature and pH of the solution were investigated and optimized with synthetic water in batch mode. A technology of defluoridation through electrochemical route has been developed[18]. The basic principle of the process is the adsorption of fluoride with freshly precipitated Aluminum Hydroxide which is generated by the anodic dissolution of aluminum or its alloys in an electrochemical cell.

In this study, fluoride removal process was infused with micro-nano bubble pretreatment. The bubble generator was used to produce bubbles inside the tank containing fluoride wastewater for 2 hours before each test and then the associated reagents were applied and given a predefined time interval to see the results.

2. Materials and methods

2.1. Materials

Wastewater was delivered by the relative company; a total of approximately 6000 L of wastewater was used in this experiment. The average Fluoride content of the raw wastewater was 30.63 ppm and COD was 101 mg/L. The supplied wastewater contained BF_3 which is molecularly big and as we all know, larger molecules are very hard to break and therefore they are less participating in reactions. Micro-nano bubbles tend to break and create high temperature.

The purpose of micro-nano bubble pre-treatment was to break this large molecule into smaller parts so it becomes more prone to further chemical treatments.

The reagents used in this experiment are;

- Poly Aluminum Chloride(PAC 11%) $[Al_2(OH)nCl_6\text{-}n \cdot xH_2O]m(m \leq 10, n=3\sim5)$
- Alum $[Al^2(SO_4)_3 \cdot nH_2O]$
- F900 $[[M](OH)_x(Cl)_y]$

Calcium Hydroxide was used to adjust the pH of the wastewater to 10.5 after micro-nano bubble pre treatment. The added $Ca(OH)_2$ reacts with the fluoride in the wastewater and precipitates as CaF_2. The polymers used in this experiment are A-polymer and A430P polymer.

2.2. Experimental procedure

Several replications were done during the experimental period. After air bubble pre treatment and $Ca(OH)_2$ injection, samples were taken in several beakers and stirred in a jar tester where after pre-defined reaction time, the reagents(PAC, F900 and Alum) were injected(Table 1).

2.3. Analytical methods

pH value was determined using Elemetron Multifunction Meter CX 401 at room temperature.

Chemical Oxygen Demand (COD) was measured according to Reactor design method(method 8000) using the spectro-photometer DR 2800.

Fluoride was measured by SPADNS method

Table 1. Five stages of the experiment

Stages	Procedures
1	- Air bubble generator was operated - Bubble outlet was inserted into the wastewater tank - Wastewater was infused with air bubble for 2 hours
2	- After air bubble pretreatment, $Ca(OH)_2$wasaddedtothewater - pH was adjusted to 10.5 by adding $Ca(OH)_2$ - Reaction time was set for 2 hours during which stirring was done at 150 rpm
3	- After 2 hour reaction, samples were taken into 1 L beakers - Reagents(PAC 11%/Alum/F900) were added one in each beaker by pipette - Reagents were injected until pH became 6.5 - Samples were stirred at 150 rpm for 1 hour
4	- After 1 hour reaction, 4-5 mL/L of polymers(A-polymer/A430P polymer) were injected in the beakers - Samples were stirred at 150 rpm for 30 minutes
5	- Laboratory stirrer was stopped - After 20 minutes of settling, samples were collected and analyzed for fluoride and COD

(method 8029) using the same spectrophotometer. Samples were diluted as required for measurement. This method for fluoride determination involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to the fluoride concentration. This method is accepted by the EPA for NPDES and NPDWR reporting purpose when the samples have been distilled[19]. The reported concentration for each sample is the average of 3 times measurement.

3. Results and Discussion

After the air bubble pre-treatment, $Ca(OH)_2$ was added to the wastewater until pH 10. After this addition, pH was observed to be increasing a little throughout the 2 hour reaction period. An optimal pH for $Al(OH)_3$ formation is in the range of 5-7[20]. Reagents were injected minding the pH barrier of 6.5, approximately 400 to 600 ppm of reagents were required per liter of sample to attain that level of pH. Polymers were added at the rate of 4-5 mL/L, it was observed that 4 mL/L is optimum for the reaction for both A-polymer and A430P polymer. The settling process sometimes took a little bit more time than the pre defined 20 minutes. But overall 20 minutes of settling time was observed to be enough for 1 L of sample. Throughout the entire experimental days, temperature was 19 to 25 degree Celsius.

From the experimental data and comparison charts above, it seems that air

Table 2. Experimental data after analysis

Reagents	Polymers	Without air bubble pretreatment	With air bubble pretreatment	Percentage Removed without air bubble pretreatment (%)	Percentage Removed with air bubble pretreatment (%)
Average Fluoride content measurement (ppm)					
PAC 11%	A-Polymer	9.688	7.188	68.37	76.53
F900		9.313	7.125	69.6	76.74
Alum		11.44	12.19	62.65	60.2
PAC 11%	A-430P	8.75	7.063	71.43	76.94
F900		10.56	7.938	65.52	74.08
Alum		13	12.5	57.56	59.19
Average COD content measurement (mg/L)					
PAC 11%	A-Polymer	45.5	37.25	54.95	63.12
F900		45.75	36.75	54.7	63.61
Alum		45.5	41.5	54.95	58.91
PAC 11%	A-430P	47.5	37.25	52.97	63.12
F900		45.5	38	54.95	62.38
Alum		43.25	35.75	57.18	64.6

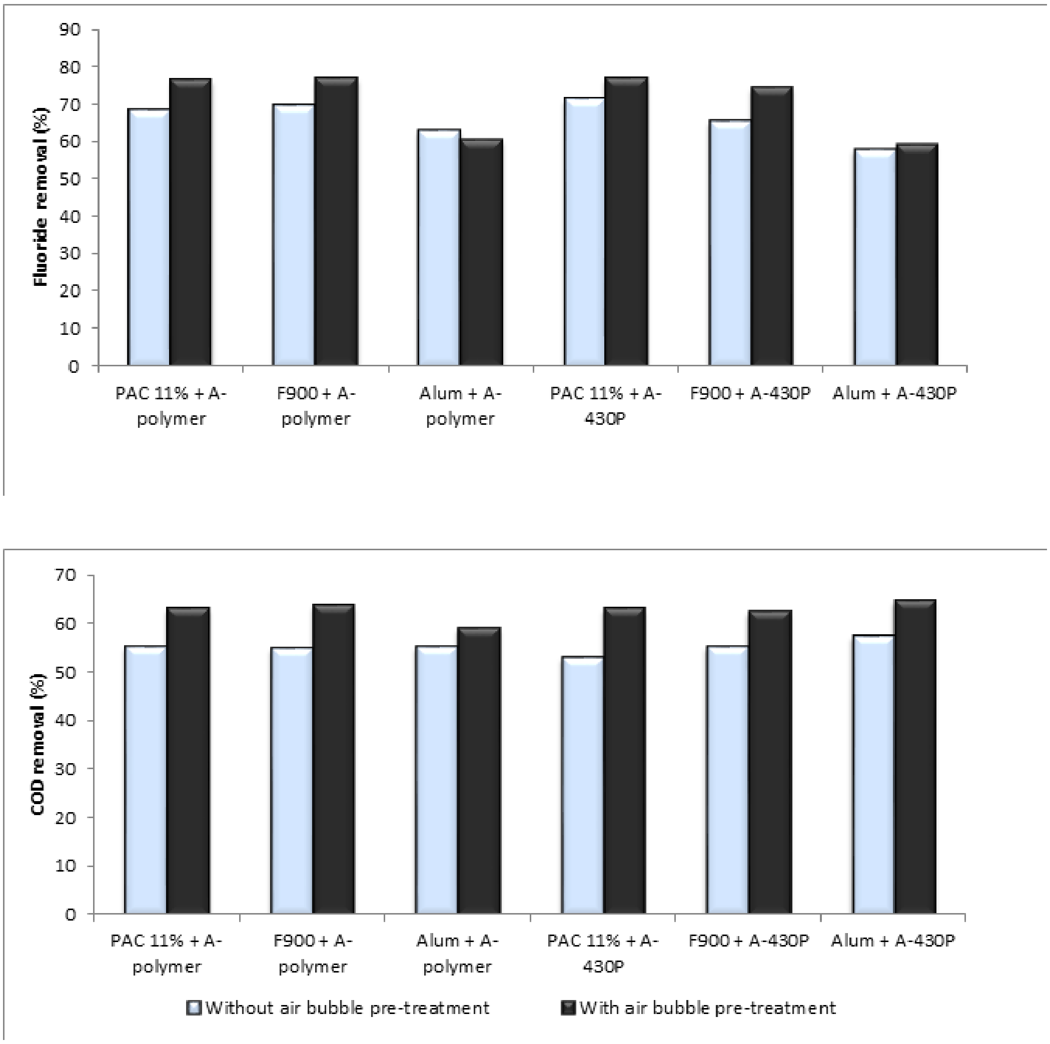

Fig. 1. Comparison chart of percentage fluoride removal(upper) and percentage COD removal(lower).

bubble pre-treatment serves well in case of reducing fluoride and COD content from wastewater(Fig. 1). Except the combination of Alum and A-polymer, fluoride removal percentage is higher in every case for the air bubble pre-treated wastewater and in case of COD removal it is obvious from the comparison chart that the results of air bubble pre-treated wastewater are more satis- factory than without pre-treatment. Up to 76.94% fluoride and 64.6% COD removal was achieved using our pre-treatment process, whereas, without air bubble pre-treatment, lower removal of fluoride and COD was observed. In case of fluoride removal, performance of the reagents PAC 11% and F900 (more than 76% removal) are very good with air bubble pre-treatment compared to that of Alum(64% removal). The effect of both polymers (A-polymer and A430P) is somewhat same in response to the reagents added. The combination of PAC 11% and A430P polymer seems to have a higher fluoride removal percentage than the other combinations (76.94%). But in case of COD removal, the combination of Alum and A430P polymer was observed to be the best(64.6%).

4. Conclusion

From this study, it can be seen that removal of fluoride from industrial wastewater assisted by micro-nano bubble pre-treatment process has a higher removal percentage than a process that is not assisted by this pre-treatment technology. The following conclusions may be drawn -

1) The optimum pH range for $Al(OH)_3$ formation is 5-7. In this study, we maintained the pH at 6.5 by adding the reagents(PAC 11%, F900, Alum). Approximately 400 to 600 ppm reagents were required to attain pH 6.5.
2) The performance of both polymers (A-polymer, A430P polymer) are approximately same for all the reagents.
3) Polymers were added by 4 mL/L and 5 mL/L quantity. From this study it is obvious that 4 mL/L polymer is sufficient for the reaction environment.
4) The combination of PAC 11% and A430P polymer with air bubble pre-treated wastewater seems to have a higher fluoride removal percentage than the other combinations(76.94%).
5) In case of COD removal, the combination of Alum and A430P polymer with air bubble pre-treated wastewater was observed to be the best(64.6%).
6) The 1 hour reaction time for the reagents was optimum.
7) Settling action required more than the predefined 20 minutes time.

Acknowledgement

This study was conducted with the fund by Jeonnam Green Environment Center (JNGEC) designated by the Ministry of Environment(MOE).

Table 3. Comparison between previous works

Title	Materials and method	Results
This study-fluoride removal process infused with air bubble pre-treatment process	Industrial wastewater was used. Before adjusting the pH to 10 by adding $Ca(OH)_2$, wastewater was infused with micro-nano bubble pre-treatment process for 2 hours. 1 L samples were taken in beakers. Then the reagents (PAC 11%, F900, Alum) was injected until pH 6.5. after 1 hour of reaction, 4 to 5 mL of polymers (A-polymer, A430P polymer) were added and given 30 minutes to react. After that settling and samples collection for chemical analysis was done. Fluoride was measured by SPADNS method (method 8029) using the DR 2800 spectrophotometer	The pH required for forming $Al(OH)_3$ was maintained at 6.5 throughout the experiment. Fluoride removal efficiency was found to be higher with air bubble pre-treatment process. The combination of PAC 11% and A430P polymer seems to have a higher fluoride removal percentage than the other combinations (76.94%). But in case of COD removal, the combination of Alum and A430P polymer was observed to be the best (64.6%).

Table 3. *Continued*

Title	Materials and method	Results
Fluoride removal from industrial wastewater using electro coagulation and adsorption kinetics[19]	Electro coagulation unit, some aluminum plates placed between two aluminum electrodes. Experiments were conducted in a bipolar reactor; 1.5 L samples were used and stirred at 400rpm. Fluoride measured using SPADNS reagent	Test was done at fixed potential of 30 V. Fluoride decreased with increasing time and after 5 minutes , fluoride removal efficiency was 90%, from 4.84 to 0.48 mg/L
Fluoride removal drinking water using alum-impregnated activated alumina [21]	Stock solution of 1000 mg/L was prepared. Activated alumina was impregnated with alum by adding 200 mL of 5% $NaHCO_3$ and 200 mL of 1M $Al_2(SO_4)_3 \cdot 16H_2O$ solution to 100 g of activated alumina. pH was maintained 3.4 to 3.5 by adding 0.1N HCl. A known quantity of the stock solution and the impregnated solution was taken in a 100 mL Teflon coated bottle. Experiments were carried out in a horizontal shaker at 50 rpm for 3 hours to attain equilibrium. Fluoride concentration was measured with a specific ion electrode(ISE25F) by using TISAB solution	Most of the fluoride was removed during 10-60 min and reaches to a maximum of 92% at 3 hour. Alum impregnated activated alumina can remove fluoride effectively (up to 0.2 mg/L) from water containing 20 mg/L fluoride
Treatment of high fluoride concentration wastewater by MgAl-CO_3 layered double hydroxides [22]	Equilibrium studies - 200 mL of fluoride solution with varying initial fluoride concentrations (5-2500 mg/L) mixed with 1.5 g layered double hydroxides in a 500 mL flask and agitated at 800 rpm. pH was maintained at 6 by adding 0.1 mol/L dilute nitric acid. The concentration of fluoride ions was calculated by the following equation - $q_e = \frac{C_0 V - C_e (V + V_{ad})}{m}$ Kinetic studies - 6 g of layered double hydroxides were dispersed in 800 mL of fluoride solutions with a concentration of 1000 or 1500 mg F^-/L. Aliquots (2 mL) were extracted and diluted to 50 mL. fluoride concentration was measured from this diluted samples by using the following equation - $q_t = \frac{(C_0 - C_t) V}{m}$ Where q_t is the amount of adsorbed fluoride at time t (mg/g); q_e is the fluoride loading; V is the volume of solution (L); V_{ad} is the cumulative added volume of dilute nitric acid and sodium hydroxide	The amount of adsorbed fluoride by layered double hydroxides increases with decreasing solution pH in the range 6 to 10. The maximum adsorbed fluoride was found to be 319.8 mg/g

Table 3. *Continued*

Title	Materials and method	Results
Treatment of high fluoride concentration wastewater by MgAl-CO_3 layered double hydroxides [22]	solution (L); fluoride concentration and m is the mass of adsorbent C_o (mg/L) and C_t (mg/L) are initial fluoride concentration and fluoride concentration at time t respectively; C_e is the equilibrium	
Fluoride removal from semiconductor wastewater using electro coagulation-floatation [23]	Experiments were conducted in a bipolar batch reactor with seven aluminum electrodes connected in parallel. Sample volume was 1 L and homogeneous condition was maintained by stirring at 400 rpm. Synthetic solutions were prepared by mixing stoichiometric amounts of NaF (500 mg as F) and 2.13 g $CaCl_2 \cdot 2H_2O$ with deionized water. Various amounts of Sodium Dodecyl Sulfate stock solution was added to the synthetic solution. A 100 mL volume of treated solution was sampled 5 minutes after the reaction was complete. The concentration of fluoride was measured using a specific fluoride electrode (Orion Research Inc., ion plus fluoride 9609BN, USA)	Initial fluoride concentration of the raw wastewater was 806 mg/L which was measured by ion chromatograph. The residual fluoride concentration ranged from 5 to 6 mg/L and was unaffected by Sodium Dodecyl Sulfate concentration.
Electrochemical removal of fluoride ions for industrial wastewater [20]	Desired concentrations of fluoride solution were prepared by mixing NaF with deionized water. To increase the conductivity of the solution NaCl was added to it. Influent pH was adjusted by using 1.0M NaOH and 1:5 (volume) H_2SO_4 solutions. The system consists of an electro-coagulation cell and an electro-floatation cell each with a effective area of 50 cm^2. The concentration of fluoride was measured using a specific fluoride electrode (Orion Research Inc., ion plus fluoride 9609BN, USA) according to the standard method given by APHA	Optimum pH range for $Al(OH)_3$ formation was observed to be 5 to 7. No $Al(OH)_3$ was formed below pH 2 and beyond pH 10. Optimum retention time was 20 minutes. Higher charge loading resulted in good fluoride removal efficiency. A feasible charge loading for 15 mg/L fluoride wastewater was 5F/m^3. Anions give a negative effect on fluoride removal

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