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# The effectiveness of calcium hydroxide and sodium hydroxide as neutralizer in coagulation for reducing fluoride in hazardous wastewater

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**Abstract**
The use of coagulant in Hazardous wastewater treatment containing Fluoride can decrease the pH of waste water, so calcium hydroxide and sodium hydroxide compound has been added in the process which can increase the pH value. This experiment consists of the optimum dose determination and the test phases. The optimum dose determination phase was performed by coagulation process using jar test and testing phase on pH, fluoride content, total suspended solids, total dissolved solids, and Chemical Oxygen Demand (COD). The use of calcium hydroxide and sodium hydroxide to precipitate fluoride ions in wastewater was then tested for its effectiveness. The optimum dosage of coagulant to precipitate liquid waste of Hazardous wastewater containing fluoride was 2,222 mg/L. The addition of coagulant PFS 2,222 mg/L with a neutralizing agent of calcium hydroxide 2,500 mg/L (PFS/Ca $(OH)_2$ to decrease fluoride content, total suspended solids and COD more effective than PFS 2,222 mg/L with a neutralizing agent of sodium hydroxide 1,400 mg/L (PFS/NaOH).

**Keywords:** calcium hydroxide, sodium hydroxide, coagulation, fluoride, hazardous wastewater

## Introduction

Fluoride wastes are widely produced from various industrial processes such as steel, aluminum, copper, nickel and phosphate. The use of pesticides containing fluoride also affects fluoride in the soil source.

One of the main sources of fluoride is in drinking water, other sources are found in foods, dental products such as toothpastes and mouthwashes, and fluoride dust and smoke from industries using fluoride in both salt and hydrofluoric acid [1].

Fluoride is an electromagnetic substance and not present in a state free in nature, but only present in the form of fluoride salts. Natural waters usually have fluoride contents of less than 0.2 mg/L. In groundwater the levels of fluoride reach 10 mg/L and in the sea waters around 1.3 mg/L.

Wastewater quality standard of health activities of Fluoride concentration is maximum 2 mg/L [2]. Fluoride is a hazardous and toxic waste due to its corrosive nature. Its concentrations in excess of 1.7 mg/L can result in dyeing of tooth enamel known as mottling, and in excessive levels can cause bone damage.

Poly Ferric Sulfate (PFS) is one of the chemical coagulants that cause the destabilization of the particle negative charge in the suspension that can help clear the waste water [3]. The addition of PFS into the wastewater may decrease the pH, so in processing it should be added calcium hydroxide and sodium hydroxide compounds which can raise the pH value. In general, the neutralization process is used to neutralize liquid waste that is too acidic or alkaline. However, in some types of wastewater containing dye, neutralization can reduce or even completely eliminate the color. Chemicals to neutralize the pH are selected by considering the price, the obtaining convenience and storage safety in addition to its effectiveness. Commonly used neutralizing chemicals are sodium hydroxide and calcium hydroxide [4].

Calcium hydroxide (CaOH) and sodium hiroxide (NaOH) are also used to precipitate fluoride ions in wastewater which are then tested for effectiveness before they are made on a large scale and applied to waste treatment. The nature of NaOH as a coagulant can make the colloid particles unstable, so that the particles are ready to form a flock.

NaOH can bind impurities that contain lots of positive ions, so they can bind to larger flock and faster precipitation processes [5].

The use of sodium hydroxide in the waste treatment of fluoride with calcium chloride coagulant can reduce the fluoride content of 99.72% [6].

The use of Calcium Hydroxide in the area of environmental health includes wastewater treatment. CaOH can be useful as a hardness-reducing agent, neutralize acidity, and minimize levels of silica, manganese, fluoride and other organic materials [7]. CaOH is a strong base because it is perfectly ionized, but this base has a smaller solubility than the solubility of NaOH. $Ca(OH)_2$ solution is also a medium strength base compared to NaOH [8].

The purpose of this study is to compare the effectiveness of Calcium Hydroxide and Sodium Hydroxide as a neutralizer in reducing fluoride levels in the hazardous wastes.

## Experimental

### Material and measurement

The materials used are hazardous inorganic wastewater from Batching Pit 2 pond (BBP waste), industrial fluoride waste, Poly Ferric Sulfate (PFS), Calcium Hydroxide, Sodium Hydroxide, and Polyacrylamide (Megafloc TM AP 100 Series).

The chemicals used were anhydrous sodium fluoride, glacial acetate acid, sodium chloride, Cyclohexyl diamine the thraacetate (CDTA), sodium hydroxide, calcium hydroxide, orange polyacrylamidamethyl, demineralized water and COD reagents (HACH) that consist of potassium dichromate, silver sulfate, concentrated sulfate and mercury sulfate. Tools used including HACH DR 2800 visible spectrophotometer, Ion Selective Electrode Meter, Mettler Toledo Seven Easy conductor, COD HACH DRB 200 reactor, Mettler Toledo analytical balance, Jar Test, oven, fluoride electrode, vacuum filter, compressor, stirrer, glass trophies, plastic cup, pumpkin, measuring cup, spray pumpkin, volumetric pipette, micro pipette (100-1000) µL, bulb, GFB filter paper, pH paper, stirring rod, dropper, magnetic stirrer, and tissue.

### Sampling

Fluoride samples came from companies / industries given by sampling officers. Samples of hazardous inorganic wastewater were collected by the sampling officer at the Batching Pit 2 pool at the representative point of collection. Samples were put into polyethylene plastic with a capacity of 25 liters.

### Determination of optimum dosage

Samples were added by PFS with variation concentration 1,111 mg/L, 2,222 mg/L, and 3,333 mg/L. Stirring was carried out for 1 minute at a rate of 120 rpm using a jar test stirrer and added $Ca(OH)_2$ 10% or 10% NaOH until pH 7. Samples having a neutral pH, then added by 12.5 mg/L polyacrylamide at each concentration variation PFS and stirring for 30 seconds at a speed of 120 rpm using a jar test stirrer. The sample was allowed to stand for ± 15 minutes, and then the clear solution at the top was separated from the precipitate by decantation. The same treatment was done three times. The result solution have been tested of the degree of acidity (pH), fluoride, total suspended solids, total dissolved solids, and COD.

### Examination Stage

### Degree of Acidity (pH)

The measurement of pH was using universal indicators. The indicator paper was immersed in a beaker glass containing sample or jar test result. The results are compared with the color scale on the pH paper box.

### Total suspended solid (TSS)

### Filter Paper Preparation

Vacuum filters were cleaned by rinsing 50 mL of demineralized water, and then GFB filter paper rinsed with 50 mL demineralized water. Filter paper was in the oven for 1 hour until constant weight at temperature (103-105) ºC, then cooled in desiccator. The filter paper is weighed and the value shown on the analytical balance is recorded as the weight of the empty filter paper (A).

### Sample Analysis

A filter paper was attached to a vacuum filter. The sample was 5 mL pippeted, while the jar test was 50 mL pippetted into the vacuum filter. The filter paper and residue were stirred for 1 hour at 103°C, and then cooled in desiccator. The filter paper was weighed and the value shown on the analytical balance is recorded as the weight of the filter paper + residue (B).

The calculation of Total Suspended Solid (TSS) as follows [9]:

$$TSS\ \left(\frac{mg}{L}\right) = \frac{(B-A)}{V}\ x\ 1{,}000$$

Where,

| | | |
|---|---|---|
| A | : | weight of the empty filter paper (mg) |
| B | : | weight of the filter paper + residue (mg) |
| V | : | piped sample volume (mL) |
| 1000 | : | unit conversion factor (mL/L) |

### Total dissolved solid (TDS)

Samples and the results of each jar test as much as ± 25 mL inserted into the cup glass. The electrode was rinsed with demineralized water and wiped until dry and then immersed in the sample to be measured. The values listed on the tool are recorded [10].

### Chemical oxygen demand (COD)

The samples and the results of each jar test were 1 mL pipetted, then put into a 10 mL measuring flask and dissolved with demineralized water. The solution was stabbed and homogenized. The solution was 2 mL piped and inserted into COD tube that already contains COD reagent. The COD tube was closed and shaken until homogeneous. The COD tube containing the sample was heated in a COD reactor at a temperature of 150ºC for 2 hours. The COD tube was removed after 2 hours and allowed to reach room temperature. COD concentrations were measured using visible light spectrophotometers at a wavelength of 620 nm. The blank was measured before the sample measurement.

The calculation of COD concentration as follows [11]:

$$COD\ (mg/L) = C\ x\ fp$$

Where,

C: COD concentration that was read in the instrument (mg/L)

fp: dilution factor

### Fluoride Measurement

The sample and the results of each jar test was 2.5 mL pipetted and inserted into a 50 mL volumetric flask, then dissolved with demineralized water. The solution was stabbed and homogenized. A solution of ± 9 mL was put into a 30 mL plastic cup, and then 1 mL of fluoride buffer solution was added. The electrode was rinsed with demineralized water and wiped with a tissue, and then the electrode was dipped in the sample to be measured.

The results obtained are recorded, then fluoride ($F^-$) in the sample can be calculated using the following formula [10]:

$$\text{Fluoride concentration (mg/L)} = C \times fp$$

Where,
C: fluoride concentration that was read in the instrument (mg/L)
Fp: dilution factor

The data obtained from the measured test results were fluoride, TSS, TDS, and COD compared to before and after optimum dose determination to obtain effectiveness value for decrease of fluoride content, TSS, TDS, and COD.

To find out the effectiveness of waste water treatment data obtained then calculated by using the formula as follows [12]:

$$\%Efectiveness = \frac{Ps - Po}{Ps} \times 100\%$$

Where,
$P_s$ = *Inlet* Measurement Result (Sample)
$P_o$ = *Outlet* Measurement Result (*Jar test Result*)

## Result and Discussion

### Determination of Optimum Dosage

In the optimum dose determination, the sample was conditioned to have a neutral pH value at the end of the coagulation process. Tests were performed with a varied coagulant dose of 1,111 mg/L; 2,222 mg/L and 3,333 mg/L. The addition of coagulant 2,222 mg/L can decrease pH value from 5 to 4 and 3,333 mg/L can decrease pH value from 5 to 3, while in coagulant addition 1,111 mg/L pH was fixed value that is 5. Neutralization has been done after coagulant added, resulting in a varying dose of neutralizer. Variations of PFS and neutral doses can be seen in Table 1.

**Table 1:** Dosage Variation of PFS and Neutralizer

| No | PFS Dosage (mg/L) | Neutralizer Dosage | |
|---|---|---|---|
| | | $Ca(OH)_2$ (mg/L) | NaOH (mg/L) |
| 1 | 1,111 | 1,300 | 7,00 |
| 2 | 2,222 | 2,500 | 1,400 |
| 3 | 3,333 | 2,600 | 1,800 |

The more the dosage of coagulant, the more the dosage of neutralization was added. Dosage of $Ca(OH)_2$ was added more than NaOH because $Ca(OH)_2$ solution was a medium strength base compared to NaOH solution [8].

In the coagulation process, a rapid stirring of 120 rpm for 1 minute occurs, in rapid agitation there was a uniform dispersion between the PFS coagulant and the sample to obtain a homogeneous mixture and the colloid particles contact each other and collide with each other. When it stopped slowly the contact and collision between particles were more and more often.

The contact agglomerated micro-coagulated solid dissolved solid particles into larger flock particles. The flocks settled to the bottom of a 1 liter beaker glass, so there were two layers; liquid layer over a clearer precipitate and a layer of flock deposits on the bottom of the beaker glass.

Precipitation after the coagulation process results in varying degradation of the solids. Flocks formed were separated from the liquid. Furthermore, laboratory tests have been done for pH, TSS, TDS, COD, and fluoride parameter of water that has been separated from the precipitate. The measurement of the results of the test jar can be seen in Table 2.

**Table 2:** Test Parameter Measurement of The Result of Jar Test.

| Parameter | Coagulant Adding | | | | | |
|---|---|---|---|---|---|---|
| | 1,111 mg/L | | 2,222 mg/L | | 3,333 mg/L | |
| | A | B | A | B | A | B |
| pH | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 | 7.00 |
| Total Suspended Solid (mg/L) | 54 | 30 | 10 | 29 | 33 | 42 |
| Total Dissolved Solid (mg/L) | 5,973 | 6,120 | 6,220 | 6,773 | 6,570 | 7,200 |
| COD (mg/L) | 3,130 | 3,153 | 2,973 | 3,073 | 3,220 | 3,430 |
| Fluoride (mg/L) | 12.05 | 35.70 | 10.49 | 35.60 | 12.72 | 38.93 |

Where,
A: $Ca(OH)_2$ as a neutralizer
B: NaOH as a neutralizer

Optimum dosage of PFS coagulant was considered optimal if the processed water has the best quality of water with TSS, TDS, COD, and fluoride were lowest. The best quality processed water was produced in the addition of PFS coagulant 2,222 mg/L. Coagulant dosage variations and the neutralizer type provide changes to each parameter tested.

### Total Suspended Solid

Total Suspended Solid (TSS) is one of the important parameters in wastewater caused by sludge, microorganism, and fine sand, all of which have size <1 µm. TSS of water samples serve as an indicator of the decrease of solids occurring. Determination of TSS was useful for finding out the domestic wastewater pollution strength, and also useful for determining the efficiency of the water treatment unit [12]. The effect of adding coagulant dosage and type of neutralizer to the TSS can be seen in Figure 1.

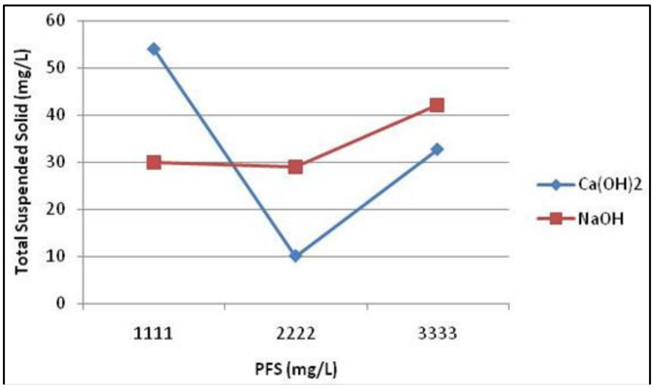



**Fig 1:** The Influence of Addition of Different Coagulant and Neutralizer to the Change of Total Suspended Solids.

The optimum condition of TSS was in the addition of PFS of 2,222 mg/L with $Ca(OH)_2$ neutralizer of 2,500 mg/L and NaOH of 1,400 mg/L. The concentrations of TSS in that condition were 10 mg/L and 29 mg/L. The higher the dosage of PFS does not guarantee a better elimination of TSS. In addition of 3,333 mg/L of PFS, an increase in TSS occurred due to the given coagulant dosage that was not optimal so that the initial dosage role for TSS turns into the impurities of the tested sample. That was due to PFS dosage that exceeds the optimum dosage causing re-stabilization of suspended substances [13].

**Total Dissolved Solid**

Total Dissolved Solid (TDS) that present in water was the reaction product of solid, liquid, and gas in water which can be either organic or inorganic compounds [14]. The effect of adding coagulant dosage and type of neutralizer to the TDS can be seen in Figure 2.

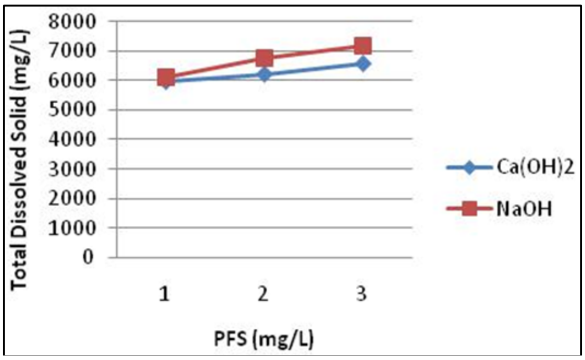



**Fig 2:** The Influence of Addition of Different Coagulant and Neutralizer to the Change of Total Dissolved Solid.

The concentration of TDS increased after coagulation and flocculation. The increase occurred because of the process of coagulation, the addition of coagulant and neutralizing agent, so that dissolved solids are in the water as a result of reaction increased the concentration. The deficit of chemical processes can lead to an increase in dissolved content in wastewater. For example, when chemicals were added to increase the efficiency of particle removal, the concentration of dissolved solids in wastewater increases [15].

**Chemical Oxygen Demand**

The COD test is an alternative to the decomposition test of some components that is stable against biological reactions or cannot be broken down by microorganisms [16]. The effect of the addition of coagulant dosage and the type of neutralizer of COD changes can be seen in Figure 3.

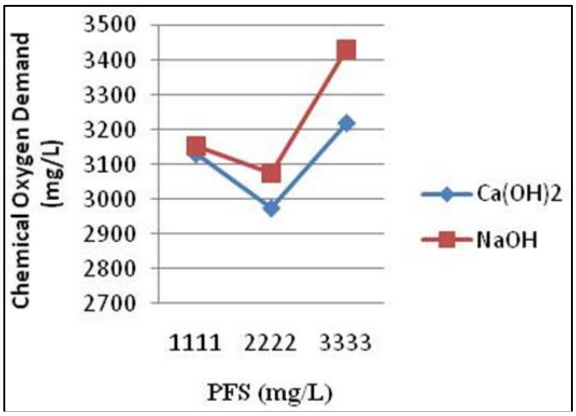



**Fig 3:** The Influence of Addition of Different Coagulant and Neutralizer to the Change of Chemical Oxygen Demand.

The optimum result was the addition of 2,222 mg/L PFS as a coagulant with 2,973 mg/L $Ca(OH)_2$ and 3,073 mg/L NaOH as neutralizers. The more precise the pH setting was given; the suspended particles and organic compounds would be bound by the PFS molecule. The reduction of organic compounds and suspended solids in the waste water caused the oxygen demand to oxidize the compound reduced and decrease COD concentration. There was saturation in addition of 3,333 mg/L PFS characterized by the formation of more sediment compared with the addition of 2,222 mg/L PFS. The addition of excess coagulant will stabilize the sediment and reduce flocculation performance. This was due to the addition of the organic material charge in the sample so that more oxygen was required to oxidize these organic materials and then reducing dissolved oxygen in the sample [17].

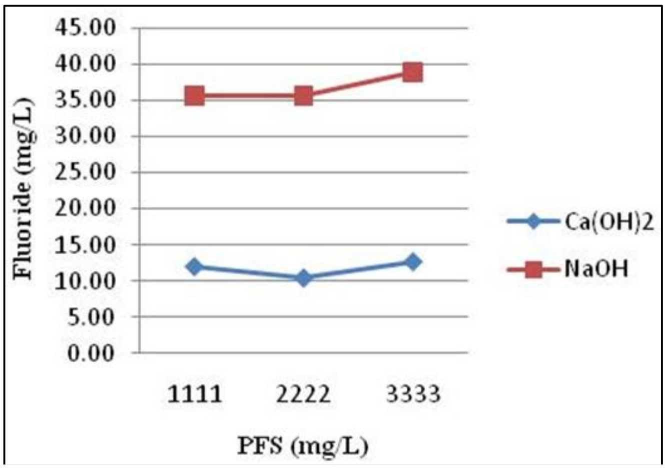



**Fig 4:** The Influence of Addition of Different Coagulant and Neutralizer to the Change of Fluoride

**Fluoride**

The influence of the addition of coagulant dosage and the neutralizer type of fluoride change can be seen in Figure 4.

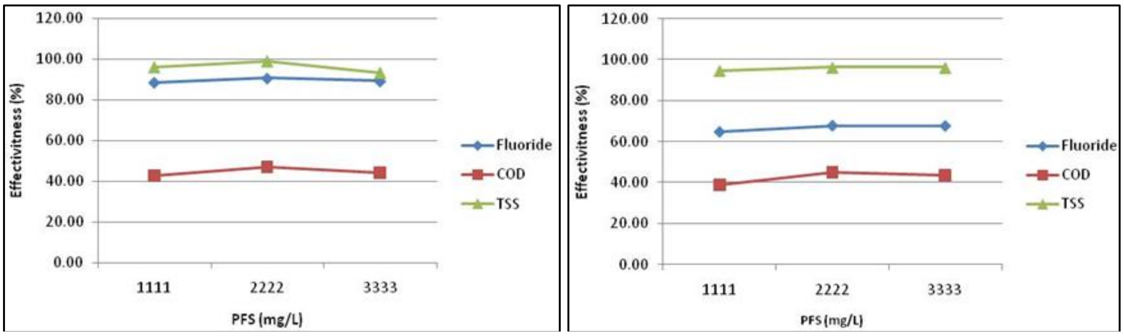
The optimum result was the addition of PFS 2,222 mg/L as a coagulant with 10.49 mg/L $Ca(OH)_2$ and 35.60 mg/L NaOH as neutralizers. Calcium hydroxide was better than sodium hydroxide to reduce fluoride concentration, because fluoride ions settle better with calcium hydroxide. Fluorides binding to monovalent cations such as NaF are soluble, whereas fluorides binding to divalent cations such as $CaF_2$ are insoluble:

$$2F^- + Ca^{2+} \rightarrow CaF_2 \downarrow$$

However, it is possible that fluoride can precipitate with $Na^+$ solution in iron (III) solution to form a crystalline white precipitate of sodium hexafluoroferrate [18]:

$$6F^- + Fe^{3+} + Na^+ \rightarrow Na_3[FeF_6] \downarrow$$

Percentage of treatment effectiveness with $Ca(OH)_2$ and NaOH as neutralizers of decreasing concentration parameters of TSS, COD, and fluoride can be seen in Figure 5.




**(a)** **(b)**

**Fig 5:** Treatment Effectiveness with: (a) $Ca(OH)_2$ dan (b) NaOH

Based on Figure 5a, the optimum dosage of PFS with $Ca(OH)_2$ in precipitating wastewater containing fluoride was 2,222 mg/L. The optimum dosage of PFS with $Ca(OH)_2$ has a better percentage of fluoride waste reduction of 90.50% than PFS with NaOH (67.75%) can be seen in Figure 5. Based on Figure 5b, the optimum dosage of PFS with NaOH in precipitating wastewater containing fluoride was 2,222 mg/L. The percentage of concentration decreasing of TSS at optimum condition of PFS with $Ca(OH)_2$ (98,75%) is more effective than PFS with NaOH (96,33%) that can be seen in Figure 5.

The decrease of COD at optimum condition of PFS with $Ca(OH)_2$ (46,93%) is more effective than PFS with NaOH (45,15%) can be seen in Figure 5. COD is the amount of oxygen in ppm or mg/L which is needed to oxidize chemically, whether biodegradable or non-biodegradable materials [19]. The reduction of COD was very small or less than 50%, this is because there were still many biodegradable organic compounds in the sample which was better processed or decomposed biologically rather than chemically.

## Conclusion
The optimum dosage of PFS coagulant in precipitating hazardous wastewater containing fluoride was 2,222 mg/L. Optimal dosage of 2,222 mg/L PFS as a coagulant with addition of 2500 mg/L $Ca(OH)_2$ as a neutralizer showed optimal results on the TSS, COD, and fluoride.

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