Flocculation of Reactive Blue 19 (RB19) using Alum and the Effects of Catalysts Addition

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Abstract—There are a variety of primary coagulants which can be used in a water treatment plant. One of the earliest, and still the most extensively used, is aluminum sulfate, also known as alum. Aluminum Sulfate (Alum) is one of the most commonly used flocculant in waste water treatment processes. Effectiveness of Alum in flocculation process is determined by many factors such as the effluents pH, flocculent dose as well as the use of catalyst to improve efficiency rate of flocculation. Hence special attention to these factors especially the use of catalyst has been brought about by this study. Experiments were carried out using Reactive Blue 19 Dye as the contaminant of waste water and two catalysts namely Calcium Hydroxide (CaOH₂) and Poly Aluminum Chloride (PACl) were evaluated. The results obtained proved that indeed after addition of catalysts, removal efficiency rates of Alum can be increased up to 25% using Calcium Hydroxide and up to 35% using Poly Aluminum Chloride compared to Alum alone. The optimum conditions for this study were at pH 5.5 ~ 7.5, 300 mg/L of Alum 30 seconds of rapid mixing time with 300 rpm , 30 rpm of mixing rate for 5 minutes and 30 minutes of settling time. Moreover, Alum showed the highest performance under these conditions and using 50 mg/L PACl as catalyst with 98.52% of COD reduction and 90.60% of color reduction. In conclusion, Alum with the support of PACl as catalyst is an effective coagulant, which can reduce the level of COD and Dye Color in Reactive Blue 19 contaminated wastewater.

Keywords—Alum, Reactive Blue 19, Calcium Hydroxide, Poly Aluminum Chloride and Flocculation.

1. INTRODUCTION

Flocculation is the process of forming larger agglomerates of particles in suspension or of small agglomerates already formed as a result of coagulation through high molecular weight polymeric materials.¹ Flocculation is used in applications such as water purification, sewage treatment, cheese production, and brewing. It is also used in surface and physical chemistry, biology, and civil engineering. Flocculent describes a chemical or substance that promotes flocculation and usually has a positive charge.² Flocculation occurs when small particles in a solution lose their repelling forces and begin to attract one another. The small particles then bond together to form “flocks” or “flakes.” Under most circumstances, a flocculent is necessary to begin the flocculation process. The most common flocculents are iron, aluminum, magnesium, and calcium. When flocks are fully formed, they can be removed from the solution they are in through traditional filtration methods.³

Example:

Aluminum:

Simple: \[ \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \] (using for experiment)

Double: \[ \text{AlK}_2(\text{SO}_4)_2 \cdot 18\text{H}_2\text{O} \] and \[ \text{Al(NH}_4)_2(\text{SO}_4)_2 \cdot 18\text{H}_2\text{O} \]

Iron: \[ \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \] and \[ \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \]

Hydrolysis process of \[ \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \]

After put alum into waste water, hydrolysis reaction occurs as follows

\[
\begin{align*}
\text{Step 1} & : \quad \text{Al}^{3+} + \text{H}_2\text{O} = \text{Al(OH)}^{2+} + \text{H}^+ \\
\text{Step 2} & : \quad \text{Al(OH)}^{2+} + \text{H}_2\text{O} = \text{Al(OH)}_3 + \text{H}^+ \\
\text{Step 3} & : \quad \text{Al(OH)}_3 + \text{H}_2\text{O} = \text{Al(OH)}_3 + \text{H}^+ \\
\text{Total} & : \quad \text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 3\text{H}^+ \\
\text{General reaction} & : \quad \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{H}_2\text{SO}_4
\end{align*}
\]

The attractive forces between the flocculation substance and the pollutants in wastewater are the force Vander Walls, creation of solid particles with larger size and easily settled down by the gravity. With flocculation process, no chemical reaction occurs which absorbs only physical.

Influence pH to the flocculation process in using \[ \text{Al}_2(\text{SO}_4)_3 \] .

- \( \text{pH} < 4.5 \): Flocculating process will not occur
- \( 5.5 < \text{pH} < 7.5 \): good for flocculating process
- \( 7.5 < \text{pH} \): decreased efficiency
Reactive Blue 19 (RB19) was chosen for this study because it is most commonly used material for dying cotton, wood, and silk with molecular weight 626.54 corresponds to 2-(3-(4-Amino-9,10-dihydro-3-sulpho-9,10-dioxoanthracen-4-yl)aminobenzenesulphonyl)vinyl)disodium sulphate. The structure of the Reactive Blue 19 is given as below.[4]

![Molecular Structure of Reactive Blue 19 (RB19)](image)

**Fig.1: Molecular Structure of Reactive Blue 19 (RB19)**

### II. MATERIALS AND METHODS

#### 2.1 Sample preparation and materials

A 1000ppm stock solution of RB19 was used to prepare 20 liters of 10ppm concentration waste water. After about 10 mins of homogenous mixing, 1-liter sample was immediately transferred to each of the Jars of the Jar Test Equipment.

#### 2.2 Flocculent and catalysts preparation

Stock solution of Aluminum Sulfate (Alum) should be prepared before starting the experiment. 100 g of Alum was pulverized and dissolved to 1 liter in a volumetric Flask and is well shaken to ensure that the Alum is well dissolved. Calcium Hydroxide and PolyAluminum Chloride were prepared from reagent bottles and weighted with an Analytical Balance starting from 25mg for Ca(OH)₂ with 25mg increments and 50mg for PACl with 10mg increments respectively.

#### 2.3 Jar Test

A conventional jar test apparatus was used in the experiments to coagulate sample of RB19 solution by using Alum, Alum with Ca(OH)₂ and Alum with PACl. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. Besides, the sample of wastewater was adjusted from the initial pH 3.6 to pH about 7.5 in the experiments due to flocculation will not occur in an acidic aqueous phases. The pH was controlled by adding either strong acid (HCl) or strong base (NaOH). Before fractionated into the beakers containing 1L of solution each, the samples of wastewater were mixed homogeneously. Then, the samples ought to be measured for Absorbance and COD for representing an initial concentration. After the desired amount of Alum was added each of the solutions, the beakers were agitated at constant mixing time and speed, which consist of rapid mixing (300 rpm) for 30 seconds and slow mixing (30 rpm) for 5 minutes. After the agitation being stopped, the suspension was allowed to settle for 30 minutes. Finally, a sample was withdrawn using a pipette from the top inch of supernatant for Absorbance and COD measurements which representing the final concentration. All tests were performed at an ambient temperature in the range of 26-30°C. In the experiment, the study was conducted by varying a few experimental parameters, which were Alum dosage (100-500 mg/L) and Catalyst, for Ca(OH)₂ dosage (25-150 mg/L) and PACl dosage (10-50mg/L) in order to study their effect in flocculation and obtain the optimum condition for each parameter as well as the best catalyst to be used.

#### 2.4 Data Analysis

The COD test was performed by colorimetric method using HACH Model DR/890 Colorimeter and HACH COD Vials High Range (HR). It is used to measure the oxygen demand for the oxidation of organic matters by a strong chemical oxidant which is equivalent to the amount of organic matters in sample. Moreover, Absorbance was measured by using UV-VIS Spectrophotometer SP-300 Plus which the sample was filled into a sample cell and put into the cell holder for measurement. While the pH of wastewater was measured by using a digital Horiba pH meter F-21. The pH meter was calibrated by using buffer solutions of pH 4.0 and pH 7.0 before starting the experiments.

### III. RESULTS AND DISCUSSIONS

Studies on the effects of Alum dosage and the use of Catalysts are the experiments which were conducted in order to investigate the optimum capacity of Alum in flocculation process. Since the Chemical Oxygen Demand (COD) level in RB19 contaminated wastewater is considered as the most important parameter, so it has been used as the indicator on the flocculation capacity of Alum in these experiments by supporting with other important parameter which is RB19 concentration in terms of absorbance.

#### 3.1 Effect of Alum dosage

Dosage was one of the most important parameters that has been considered to determine the optimum condition for the performance of Alum in flocculation. Basically, insufficient dosage or overdosing would result in the poor performance in flocculation. Therefore, it was crucial to determine the optimum dosage in order to minimize the dosing cost and obtain the optimum performance in treatment. The effect of dosage was analyzed at pH 7.5, 300 rpm of mixing rate for 30 seconds and 30 rpm of mixing rate for 5 minutes and 30
minutes of settling time for a range of Alum dosage which varied from 100 mg/l to 500 mg/l. Besides, the sample of wastewater was adjusted from the initial pH of 3.6 to pH 7.5 due to flocculation will not occur in acidic aqueous phases.[5]

![Color andConcentration per Alum Dose](image1)

![Effect of Alum on RB19 Color Removal Efficiency (%)](image2)

![COD Concentration per Alum Dose](image3)

![Effect of Alum COD Removal Efficiency (%)](image4)

Fig. 2: Effects of Alum dosage on (a) Color and Concentration (b) Color removal efficiency (c) COD Concentration (d) COD Removal Efficiency.

The results were presented in Figure 2(a) which showed the effects of Alum dosage on Color in terms of Absorbance and Concentration of RB19. While Figure 2(b) showed the effects of Alum dosage on RB19 color removal efficiency in percentage reduction. Figure 2(c) showed the effects of Alum dosage on COD concentration in mg/L. While Figure 2(d) showed the effects of Alum dosage on RB19 COD removal efficiency in percentage reduction.

From the jar test experiment, Removal efficiency for both Color and COD will be increased when amount of Alum is increased, however efficiency will increase to a point that the increase is insignificant, even if addition of Alum dosage is done. For the Alum dosage of 300 mg/L, Alum recorded the optimum reduction of parameters, which were the reduction of 84.57% and 68.45 % for Color and COD respectively. Therefore, the optimum Alum dosage in this research was 300 mg/L.

3.2 Effect of Catalysts

Addition of catalysts Calcium Hydroxide (Ca(OH)₂) and PolyAluminum (PACl) was evaluated using a controlled dosage of Alum which is 300mg/L. The same conditions apply for the rotational stirring speed, agitation and settling time from previous experiment. The range of dosage used for Ca(OH)₂ is from 25mg/L to 150 mg/L with 25mg/L increments while for PACl is from 10mg/L to 50mg/L with 10mg/L increments. pH level is also controlled by adding either strong acid (HCl) or strong base (NaOH).
Figure 2. Effects of Catalysts on Color and Concentration for (a) Ca(OH)\(_2\), (b) PACl, COD removal for (c) Ca(OH)\(_2\), (d) PACl and Comparison of Ca(OH)\(_2\) and PACl on (e) Color removal efficiency and (f) COD removal efficiency.

The results were presented in Figure 3(a) which showed the effects of addition of Ca(OH)\(_2\) on Color in terms of Absorbance and RB19 concentration. While Figure 3(b) showed the effects of addition of PACl dosage on Color in terms of absorbance and RB19 concentration. The effects on COD removal for addition of Ca(OH)\(_2\) and PACl is shown in Figure 3(c) and 3(d) respectively. Figure 3(e) and 3(f) showed a comparison between Ca(OH)\(_2\) versus PACl in terms of Color and COD Removal efficiencies.

From the jar test experiment, the curves for the both Color and COD graphs were decreasing as catalyst dosage is increased. Removal efficiency for both Color and COD will be increased when amount of catalysts is increased, however efficiency will increase to a point that the increase is insignificant, even if addition of catalyst dose is done. For
the Ca(OH)$_2$ dosage of 100 mg/L, Ca(OH)$_2$ recorded the optimum reduction of parameters, which were the reduction of 95.03% and 78.96% for Color and COD respectively. For the PACl dosage of 50mg/L, PACl recorded the highest reduction of parameters, which were the reduction of 98.52% and 90.60% for Color and COD respectively. Therefore, the best catalyst to support Alum in flocculation process is PACl with a dosage of 50mg/L.

**IV. CONCLUSION**

Removal efficiency both of Color and COD will be increased when amount Alum is increased however efficiency will increase to a point that the increase is insignificant, even if addition of Alum dosage is done. With the use of Alum alone as the flocculent, the speed of removed color is faster than COD. For example with 500mg Alum, color removal efficiency is 84% and COD is 68%. With the support of catalyst Ca(OH)$_2$, the treatmetability of Alum can be improved up to around 22% for concentration and 25% for COD. Ca(OH)$_2$ produced high sludge volume, so only use Ca(OH)$_2$-like catalyst for Alum, it is not recommended to use Ca(OH)$_2$ alone in treatment by flocculation. In using large amount Ca(OH)$_2$, pH will increase and probably above 7.5, adjustment of pH should be done to promote flocculation process. With the use of PACl as catalyst, the treatment ability of Alum can be improved up to around 35% for concentration and 37% for COD. When using PACl, use only a small amount to make the removal efficiency increase significantly for both Color and COD. PACl is able to create the larger flocks, the polluting matter can branch this flocks and aids for settling. It is advantageous to use PACl to shorten the treating time and consequently save construction costs (tank, barrel... smaller). PACl is not a chemically corrosive, so it is good for equipments in the treatment process. In conclusion, using PACl instead of other chemical in flocculation is recommended.

**REFERENCES**


