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Impact of Chemical Coagulants for *Oscillatoria* sp. Removal from Raw Water on Chemical Coagulation Process

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Abstract: Growing *Oscillatoria* sp. in freshwater causes several poisoning episodes of domestic livestock animal and human. The chemical coagulation of raw water using chemical coagulants is very simple and requiring less investment cost on equipment. These experiments used alum and PACl (Polyaluminium chloride) with alum as chemical coagulants for *Oscillatoria* sp. removal. The *Oscillatoria* sp. was prepared from Molecular and Cell Laboratory of Thailand Institute of Scientific and Technological Research and grown in BG-11 medium. The samples of treated water use chemical coagulation test to verify their efficiency of *Oscillatoria* sp. cells removal from the synthetic raw water. The results show that the chemical coagulation using alum coagulant and PACl with alum coagulants produces a high efficiency in *Oscillatoria* sp. removal. However, the PACl with alum coagulants provided the best *Oscillatoria* sp. removal efficiency and the low amount of chemical coagulants for *Oscillatoria* sp. removal process. The PACl with alum doses at 1:10 by weight, provides the best *Oscillatoria* sp. removal efficiency at 97%. While, the best *Oscillatoria* sp. removal efficiency of alum dose at 90 mg/L, is 98%. It can be concluded that the PACl with alum doses as the combined chemical coagulant provided the highest efficiency at the lowest amount of chemical coagulants used.

Keywords: *Oscillatoria* sp., Chemical Coagulation, Alum, PACl, Chlorophyll A

Introduction

Algae are aquatic plants and photosynthetic that utilize inorganic nutrients such as phosphorus and nitrogen. Cyanobacteria, also known as blue-green algae, are a morphologically diverse group of photosynthetic prokaryotes that occupies a wide range of niches, from freshwater to hydrothermal vents. Some cyanobacteria produce toxins, called Cyanotoxins. Their most common toxic cyanobacteria in freshwater or surface waters are *Oscillatoria* sp., *Microcystis* sp., *Anabaena* sp., *Lyngbya* sp., *Aphnizomenon* sp., *Schizothrix* sp. and *Nostoc* sp. The toxicity cannot be excluded for the further species and genera (WHO, 1998). About 75% of all cyanobacteria sample contain toxin, it is the huge conglomerations of cells that present a great concern of large blooms development in summer (Chorus *et al*., 2000). The toxin production of cyanobacteria creates a risk on human and animal health. Several poisoning episodes of domestic animals and livestock have been associated with the occurrence of cyanobacteria blooms in surface waters used for drinking (Stewart *et al*., 2008).

Oscillatoria sp. is one kind of cyanobacteria. The *Oscillatoria* sp. blooms occur in freshwater. The growth of *Oscillatoria* sp. tends to occur in late summer when there are high concentrations of nutrients, particularly phosphorus, high water temperature, long hydraulic retention time and stable water body stratification (Chorus and Bartram, 1999; Villareal and Capenter, 2003). Due to these characteristics, *Oscillatoria* sp. trend to occur more often in reservoirs, lakes, ponds and dams (Pumas *et al*., 2011). The *Oscillatoria* sp. growth can be increasing because of the nutrients in the water bodies that are influenced by the fertilizer and chemical fertilizer carried by discharges of runoff or subsurface infiltration of groundwater (Naz *et al*., 2015).

The concentration of *Oscillatoria* sp. was about 4,500 cell/mL. Even a very low concentration of *Oscillatoria* sp. in water (e.g., a few nanograms per liter) can cause taste and odor in water that are associated with adverse human health effects (WHO, 2015). These tastes and odors can lead to the complaints from the customers or result in consumers using an aesthetically more acceptable, but potentially less safe, drinking-water source in the Southern Region Industrial Estate, Songkhla Province, Thailand.

The chemical coagulation can be an effective method for algae removal, although care must be taken to remove these organisms without disrupting the algae cells. The general chemical coagulation does not appear to cause the release of algae toxins, when the oxidants are not added (Carmichael, 2001). An effective method for removing intact cyanobacteria cells from drinking water is the coagulation with iron salts and alum followed by conventional flocculation and sedimentation (Drikas *et al*., 2001). Aluminum sulfate or alum is the most commonly used chemical coagulant and is easy to handle and apply and produces less sludge than lime.

The aim of this work is to test the chemical coagulants used for removing the *Oscillatoria* sp. from the synthetic raw water for water supply using jar test. The jar test is used to identify the most adapted mix of chemical coagulants and concentrations for coagulation-flocculation. The batch the test, using several identical jars with the same volume and concentration of feed, are used in this study. The results focus on the removals of chlorophyll A and algae cell.

Experiments

Microorganism

The *Oscillatoria* sp. (Fig. 1) culture used in this study was collected from Thailand Institute of Scientific and Technological Research. Pure culture was grown in BG-11 medium containing $NaNO_3$ (1.5 g/L), K_2HPO_4 (0.04 g/L), $MgSO_4{\cdot}7H_2O$ (0.075 g/L), $CaCl_2{\cdot}2H_2O$ (0.036 g/L), citric acid (0.006 g/L), ferric ammonium citrate (0.006 g/L), EDTANa$_2$ (0.001 g/L), Na_2CO_3 (0.02 g/L) and trace metal mix 1 mL/L. The composition of trace metal mix is H_3BO_3 (2.86 g/L), $MnCl_2{\cdot}4H_2O$ (1.81 g/L), $ZnSO_4{\cdot}7H_2O$ (0.222 g/L), $Na_2MoO_4{\cdot}2H_2O$ (0.39 g/L) and $CuSO_4{\cdot}5H_2O$ (0.079 g/L), Cu $(NO_3)_2{\cdot}6H_2O$ (0.0494 g/L). Figure 2 shows the *Oscillatoria* sp. cultivation.

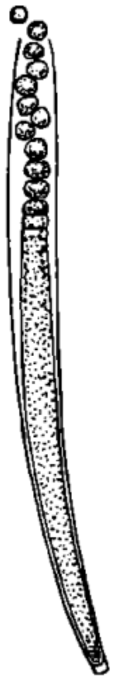

Fig. 1: The *Oscillatoria* sp. (Chorus and Bartram, 1999)

Fig. 2: The *Oscillatoria* sp. cultivation

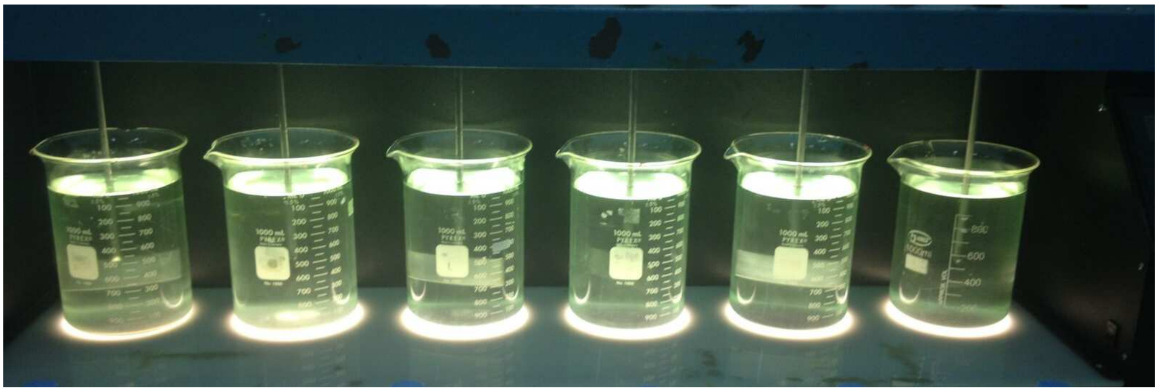

Fig. 3: The chemical coagulation

Table 1: The characteristics of synthetic raw water with *Oscillatoria* sp. cell

	Amount of *Oscillatoria* sp. (cell/mL)		
Characterisation	5,000	10,000	15,000
1. pH	7.2-7.4	7.0-7.2	7.2-7.5
2. Chlorophyll A (mg/m^3)	97.4-105	197-214	252-342
3. Alkalinity (mg/L as $CaCO_3$)	25-31	25-32	25-27

Synthetic Water

The synthetic raw water is prepared as per the data collected from the Southern Region Industrial Estate, Songkhla Province, Thailand. The distilled water is diluted with the high amount of *Oscillatoria* sp. The amount of *Oscillatoria* sp. in these experiments is 5,000, 10,000 and 15,000 cell/mL. The characteristics of synthetic raw water are shown in Table 1. The pH, chlorophyll A and alkalinity were analyzed for various amount of *Oscillatoria* sp. The result shows that the increasing amount of *Oscillatoria* sp. provided the increasing amount of chlorophyll A. However, the pH and alkalinity are not increased when the amount of *Oscillatoria* sp. is increased. The initial pH values of all samples are neutral because the raw water is prepared from the distilled water.

Batch Procedure

The chemical coagulation in these experiments used the jar test. It is followed the standard practice for a coagulation and flocculation testing of drinking water to evaluate the chemical dosages (APHA, AWWA and WEF, 1995). The synthetic raw water was filled in six beakers with 1 L each as shown in Fig. 3. The alum and PACl with alum as the chemical coagulants were added. The six-spindle multiple stirrer was used for mixing the contents of the six beakers. Then, the 1-min rapid stirring is occurred at 100 rpm, or the coagulation process. After rapid stirring, the 30-min slow stirring is occurred at 30 rpm, or the flocculation process. The final process is the 30-min settling, or the sedimentation process. At the end of the settling process, each beaker was carefully siphoned off so that the sediment at the bottom of the beaker will not be disturbed. Finally, the treated water is separated from the *Oscillatoria* sp. flocs.

Analytical Methods

The pH, chlorophyll A, alkalinity and algae cells of the synthetic raw water and the treated water after chemical coagulation process are analyzed. The pH is measured using a pH meter. The algae contents of the treated water are measured, indirectly using the analyzed chlorophyll A concentration, both and after the flocculation and settling processes. The chlorophyll A is measured by the spectrophotometry (Strickland and Parsons, 1972). Algae cell uses Sedwick-Rafter (S-R) counting chamber. The alkalinity is followed by the standard method (APHA, AWWA and WEF, 1995).

Results

The quantification in the synthetic raw water samples shows that the amount of *Oscillatoria* sp. was 5,000 10,000 and 15,000 cells/mL before the chemical coagulation process. The jar test is used in these experiments, for determining the parameters for flocculation and settling. The flocculation is carried out on a six-spindle multiple stirrer unit with the stainless-steel paddles. The alum doses were 40, 50, 60, 70, 80 and 90 mg/L. The ratios of PACl: Alum doses were 1:10, 3:10, 5:10, 3:20, 3:30, 3:40, 10:10 and 20:10 mg/L.

Effect of pH on the Chemical Coagulation

The *Oscillatoria* sp. presents the complex matrix of organic compounds in natural waters. The algae have important influences on many aspects of water treatment processes, including the performance of operations such as coagulation, filtration and oxidation. The mechanisms of algae removal by adding coagulants consist of two stages. First, the algae, which are colloidal material in the water, are neutralized. Second, the soluble compounds of the neutralization process are then removed due to the absorption of precipitated flocs (Randtke, 1988).

Figure 4 shows the trend of pH after the chemical coagulation using alum coagulant. The initial pH is around 7 (neutral). The pH is decreased after increasing alum dose. The increasing alum crystals due to increasing alum dose, results in an increasing of algae cell destabilization. Thus, the pH value is decreasing. The alum dose in the chemical coagulation can be explained through the double layer compression, charge neutralization, entrapment, adsorption and complexation (Matilainen *et al*., 2010). When the alum dose is increased, the pH decreases. Thus, the alum dose and pH are linked (Gone *et al*., 2008). For alum coagulation, it is a concern because alum can be toxic to aquatic species due to decreasing pH.

Figure 5 shows the trend of pH after PACl with alum coagulations. The initial pH is around 7 (neutral). When the increasing the alum dosed, the pH is decreased due to the increasing alum crystals. When increasing PACl and decreasing alum dosed, the pH is increased. The treated water is slightly neutral.

The optimization of the coagulation process occurs under an acidic condition between the isoelectric point of the coagulants such as pH 4.5-5.5 for Fe based coagulant and pH 5-6 for Al based coagulant (Sharp *et al*., 2006).

Effect of Alkalinity on the Chemical Coagulation

The trend of alkalinity after the chemical coagulation shows in Fig. 6. The trend of alkalinity is related to the alum dose and amount of *Oscillatoria* sp. cell. These results of alkalinity caused the decreasing in the pH value after increasing the alum coagulant.

The use of alum as a coagulant reduced the pH and alkalinity of water, as shown in Fig. 4 and 6. The experiment showed that the pH value was reduced after settling with alum. When alum is added, the pH and alkalinity of water tend to decrease. Because alum is added in the sample, the reaction is broken down into cations and negative ions. Aluminum ions from $Al_2(SO_4)_3$ are surrounded by water molecules, becoming $Al(H_2O)_6^{+3}$, where hydrogen ions (H^+) react with alkalinity in water. The $Al(OH)_3$ is main factor to decreases pH and alkalinity (Viraraghavan and Wimmer, 1988).

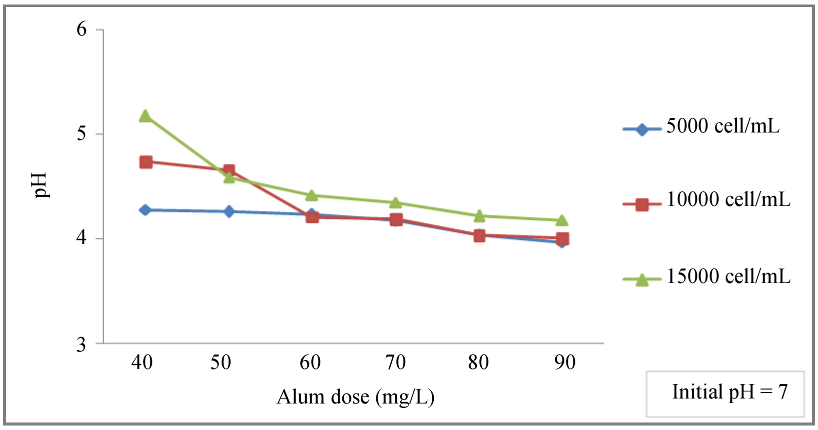

Fig. 4: Effect of alum dose on pH

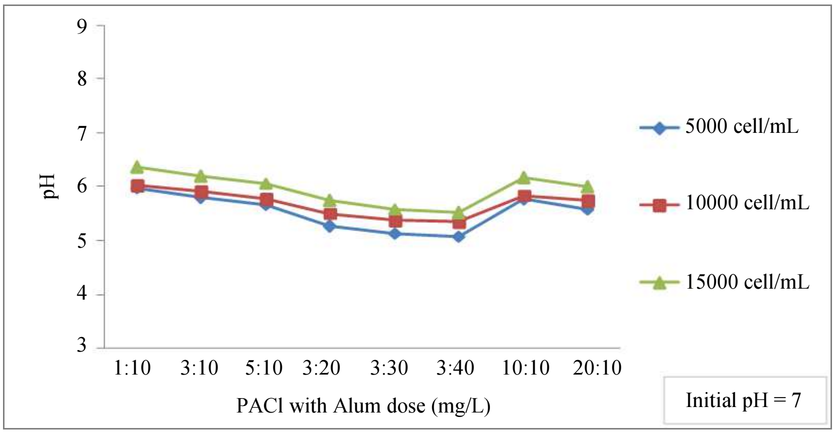

Fig. 5: Effect of PACl with alum dose on pH

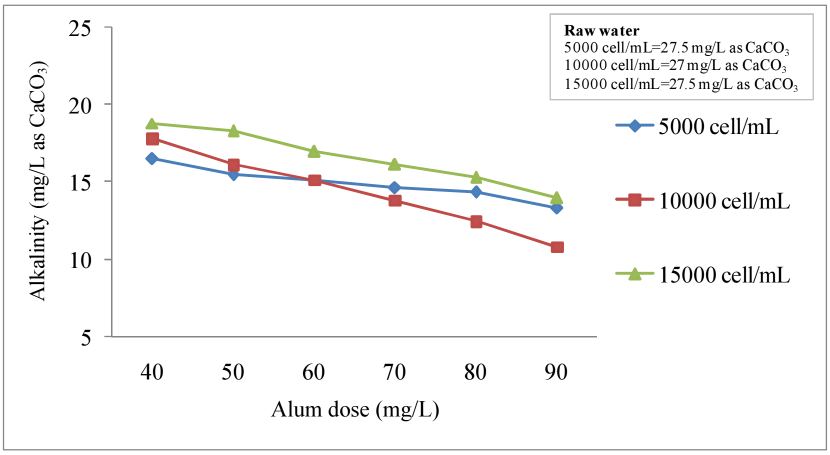

Fig. 6: Effect of alum dose on alkalinity

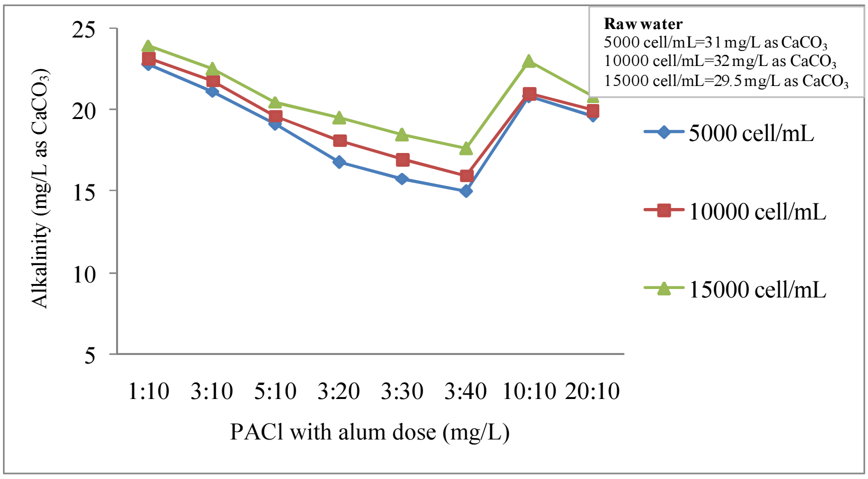

Fig. 7: Effect of PACl with alum dose on alkalinity

The effect of PACl with alum as co-coagulants on alkalinity of sample is shown in the Fig. 7. When the co-coagulant doses increased, the pH of treated water decreased. The salts of coaulant is formed aqua metallic ions as soon as the coagulant is added to the raw water. Then, the increasing ion in the system results in the decreasing of the pH value. Furthermore, the alkalinity which is related to the pH value is also decreased.

Algae Cell Removal Efficiency on the Chemical Coagulation

The alum is an inorganic coagulant. It has been and remains the most common coagulant for water treatment. In chemical coagulation, the floc quantity is determined by the charge density. The larger the algae cell size, the more floc is required for efficient chemical coagulation. The use of alum destabilizes and increases the size of the particles which will increase the algae floc size. The algae flocs are larger, rigid and settled well when adding more alum coagulant. The Fig. 8 shows the alum reduced the algae cell content effectively by flocculation and settling. The results shows that increasing the alum provided the increasing algae cell removal efficiency in all of various concentration of algae. The 40 mg/L of alum dose is the minimum alum dose, which removed 95%, 90.5% and 93.5% of algae cell for 5,000, 10,000 and 15,000 cell of algae cell/mL of raw water, respectively. The 90 mg/L of alum dose is the maximum alum dose, which provided 98% of alage cell removal for all of 5,000, 10,000 and 15,000 cell of algae cell/mL of raw water. The optimal alum concentration that is required to effect maximum flocculation depends on the amount of algae. The maximum of 90 mg of alum/L of raw water is sufficient to clarify all the *Oscillatoria* sp. examined (98% removal efficiency) for all various amount of algae cells.

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The results presented in Fig. 9 showed that the co-coagulant between PACl and alum doses could remove the algae cell. The similar *Oscillatoria* sp. removal efficiency can be achieved using PACl and alum does as co-coagulant dose and alum dose. However, the co-coagulant does is more efficient because the amount of PACl with alum does used is less than that of the alum does alone. The algae cell removal efficiency of PACl with alum does as co-coagulant does shows the same trend for all ratios. The ratio of PACl with alum dose at 1:10 by weight, provided the best algae cell removal for treating 5,000 to 15,000 cell/mL of *Oscillatoria sp*. concentration. The 1:10 ratio of PACl with alum dose contains 1 mg of PACl and 10 mg of alum in 1 L of raw water. The increasing of PACl in co-coagulant dose resulted in a lower algae cell removal efficiency. The lowest algae cell removal efficiency is at 94% for 20:10 of PACl with alum dose.

Chlorophyll A Removal Efficiency on the Chemical Coagulation

The chlorophyll is essential for the photosynthesis. The majority of chlorophyll is to absorb the light and transfer that light energy. The chlorophyll A is a large molecule that has a porphyrin ring with magnesium atom at its center. It is the pigment that interacts directly with the light requiring the reactions of the photosynthesis. Therefore, the chlorophyll A is the principal photosynthetic pigment. The chlorophyll A removal shows the same trend in Fig. 10 after the chemical coagulation using alum dose and PACl with alum dose. The optimal alum concentration that is required to effectively maximize the flocculation depends on the concentration of chlorophyll A. The flocculation and settling processes are faster when using the alum concentration that is higher than that the optimal value.

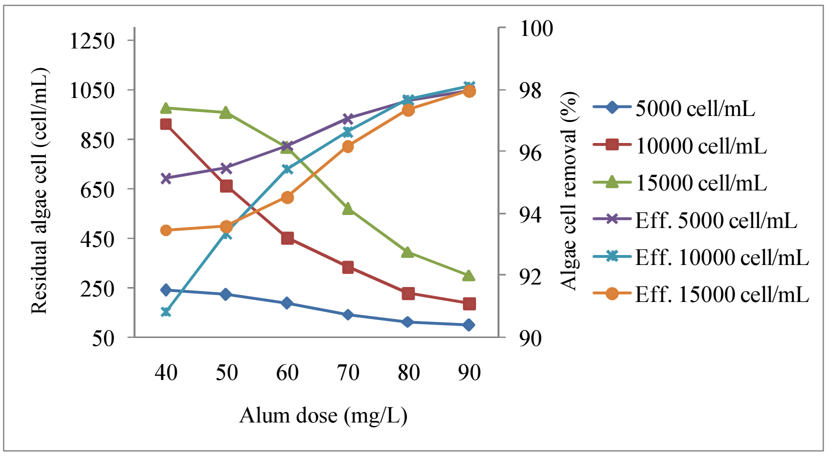

Fig. 8: Effect of alum dose on algae cell removal

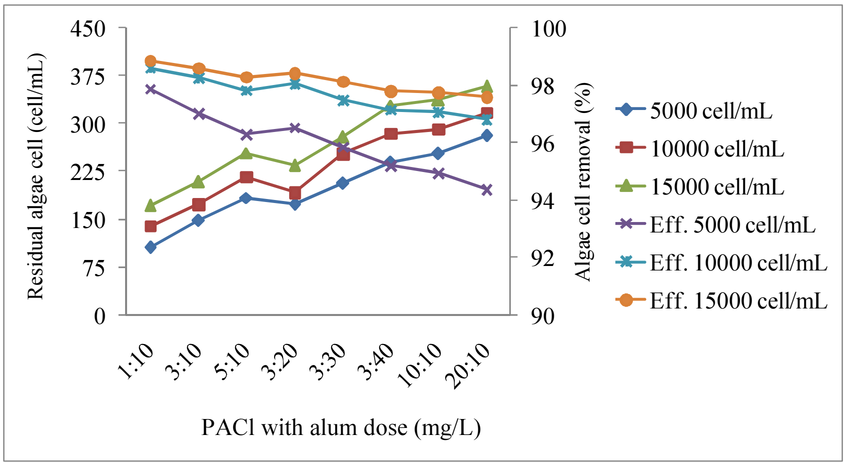

Fig. 9: Effect of PACl with alum dose on algae cell removal

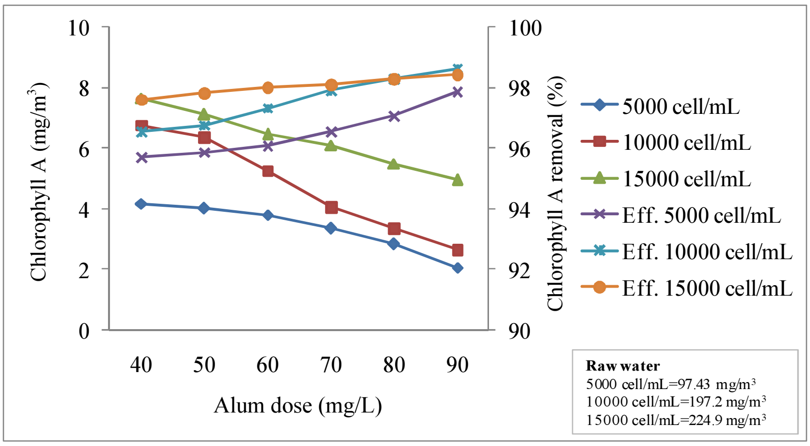

Fig. 10: Effect of alum dose on chlorophyll A removal

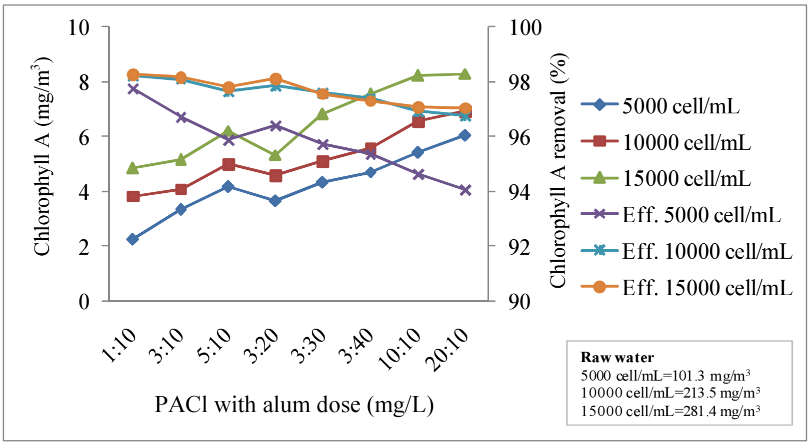

Fig. 11: Effect of PACl with alum dose on chlorophyll A removal

The results show that the three raw water concentrations of 5,000, 10,000 and 15,000 cells/mL of *Oscillatoria* sp. concentration are the most likely to remove algae in the same direction. The amount of algae and chlorophyll A decrease due to the increasing of alum. The increasing of alum breaks the stability of the algae particles. The algae can be approached and swarmed. The mechanism of the coagulation process to remove *Oscillatoria* sp. occurs when the alum is added to break the stability of the algae particles. The absorption and destruction of cell surface of *Oscillatoria* sp. will result in coagulation and precipitation when adding alum at a concentration higher than enough, the slow mixing of coagulation will produce crystalline alum. Thus, the efficiency of sedimentation increased (Ghernaout *et al*., 2010).

The chlorophyll A removal shows the same trend in Fig. 11 after the chemical coagulation using alum dose and PACl with alum dose. The ratio of PACl with alum dose is 1:10 by weight which is provided the best chlorophyll A removal for treating 5,000 to 15,000 cell/mL of *Oscillatoria* sp. concentration. The 1:10 ratio of PACl with alum dose contains 1 mg of PACl and 10 mg of alum. Thus, the operation cost of 1:10 ratio of PACl with alum dose is lower than that of 90 mg/L of maximum alum dose. When the co-coagulant dose is used the high efficiency can be achieved with less amount of dose in comparison with that of using alum dose alone. As a result, the cost of coagulant is lower than that of alum.

Discussion

PACl is a coagulant similar to alum, with a different in their the structures. The structure of PACl is larger than that of alum. Thus, PACl can contain more sediments and settle faster. Therefore, the amount required for PACl is less than that of alum. The coagulant is added to create crystals. The algae come into contact with the coagulant. Then, the coagulation process occurs. As a result, the stability of algae is destroied. From an enviromental point of views, using PACl was found to provide less environmnetal impact than using alum.

The pH and alkalinity could affect the chemistry of coagulants, particularly the speciation distribution of coagulants after the chemical coagulation (Inchio *et al*., 2013). When the chemical coagulants are increased, the pH of the treated water is decreased, because the salt ions from salt coagulant will form the aqua metallic ions as soon as the chemical coagulants. Therefore, the salt ion is related to the system causing the pH value to decrease. According to these experiment results, the chemical coagulation is effective because the amount of alkalinity is sufficient for the reaction in the chemical coagulation process.

The optimal alum concentration that is required to effectively maximum the flocculation depended on the amount of algae. The PACl is the pre-polymerized inorganic coagulants and containing high positive charge. The charge neutralization is one of algal removal mechanisms by coagulation. Thus, the better performance of PACl in the algae removal is expected. It may be concluded that the PACl with alum doses are very effective in flocculating all these verities of algae contents, with the efficacy being influenced by algae cell concentration. Flocculation presumable takes place by charging neutralization and bridging between algae cells by PACl with alum chains, as in the case of other polyelectrolytes.

Conclusion

The chemical coagulation is commonly used in the water treatment. The effective reduction of algae, silt, clay, organic matter and bacteria in surface waters by coagulation, flocculation and settling is demonstrated. Thus, the chemical coagulation is a product of choice to remove the *Oscillatoria* sp. in the synthetic raw water. The chemical coagulation using the chemical coagulants exhibits the high efficiency in *Oscillatoria* sp. removal. The results show that the optimum alum coagulant is at 90 mg/L for the chemical coagulation process. The optimum PACl: alum coagulants ratio is 1:10 by weight. The quality of treated water from PACl: alum coagulant is slightly higher than that of alum coagulant. The amount of PACl with alum coagulant dosage is significantly lower than the amount of alum coagulant dosage.

The chemical coagulation method using coagulants reduces the amount of *Oscillatoria* sp. in synthetic raw water. This simple method can be applied in the water treatment plant. In rural areas this method is economic and easy.

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Author's Contributions

Saowapak Thammasane: Designed the research plan, participated in all experiments and coordinated the data-analysis.

Thaniya Kaosol: Designed the research plan, participated in all experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and there are no ethical issues involved.

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