

Tube Flocculator

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Abstract

In order to build a complete hypothesis to support our experiments, we read three papers about PACl. They showed the main mechanisms for PACl are electrostatic patch coagulation, bridge-aggregation and precipitation/charge neutralization, and revealed that the alkalinity and size of the coagulant aggregates could influence the flocculator performance. From these hypotheses, we began the tube flocculator residual turbidity test experiment, coagulant particle size measurement and coagulant absorbency measurement. We expect that the raw water treated by the vacuum filtered coagulant would have a lower residual turbidity compared with unfiltered coagulant.

To gain a deeper understanding of how the ionic strength would influence the turbidity removal efficiency, some literature concerning about ionic strength and the effect of Ca^{2+} and Na^+ have been reviewed. They showed that, competition of Na^+ delays effective shielding of the micelles by Al^{3+} until higher Al^{3+} is present, and adding Ca would increase the content of Al_{13} which could enhance the flocculation efficiency of PACl in water treatment. In the next experiments we hope to find out the particular ions that influence flocculation efficiency over a range of coagulant doses.

We found out that decreased ionic strength in the raw water would have a negative effect on the coagulation performance, therefore we ran an ionic strength test experiment by comparing the turbidity removal efficiency of the distilled water and the tap water. From the recent work, we find there is a good linear relationship between theoretical ionic strength and conductivity and the turbidity and the PACl dosage do not influence this relationship. The research also reveals that distilled water which has the lowest ionic strength has a worse turbidity removal efficiency than tap water which has a higher ionic strength. One thing need to be noticed is that we assumed there is a linear relationship between PACl dosage and needed Na_2CO_3 to keep pH at 7.5. However, in this experiment, with the increasing of PACl dosage, the needed dosage of Na_2CO_3 decreased at first and then increased. Further experimentation is needed to reveal the relationship between Na_2CO_3 needed under different PACl dosage to maintain a constant pH at 7.5.

1 Literature Review

1.1 Alkalinity effect of coagulation with polyaluminum chlorides: Role of electrostatic patch[1]

Mechanism of electrostatic patch coagulation

Because PACl was not well neutralized at the point of optimal dosage, EPC(electrostatic patch coagulation) was introduced to explain PACl's residual turbidity removal mechanism.

EPC mainly depends on the amount and sort of species in PACl. Due to a high percentage of Al_a (monomeric species of aluminum), $PACl_0$ (The chosen B values, $[OH]/[Al]$ molar ratio, of PACl were 0, and the resulting products was denoted as $PACl_0$) was not stable after dosing and would form colloidal or amorphous hydroxide precipitate via hydrolysis. This kind of precipitate functions as electrostatic patches because it was usually positively charged and able to neutralize the negative charges on the clay particles. $PACl_{10}$, $PACl_{22}$ and $PACl_{25}$ (The chosen B values of PACl were 1.0, 2.2 and 2.5 and their resulting products were denoted as $PACl_{10}$, $PACl_{22}$ and $PACl_{25}$) which contain a lot of Al_b (polymeric species which can react with ferron rapidly) and Al_c (high polymerized or colloidal species which cannot react with ferron) were very stable and cannot be further hydrolyzed and transformed into hydroxide precipitate. The electrostatic patches could be formed through its rapid adsorption onto clay particles and subsequent aggregation and rearrangement.

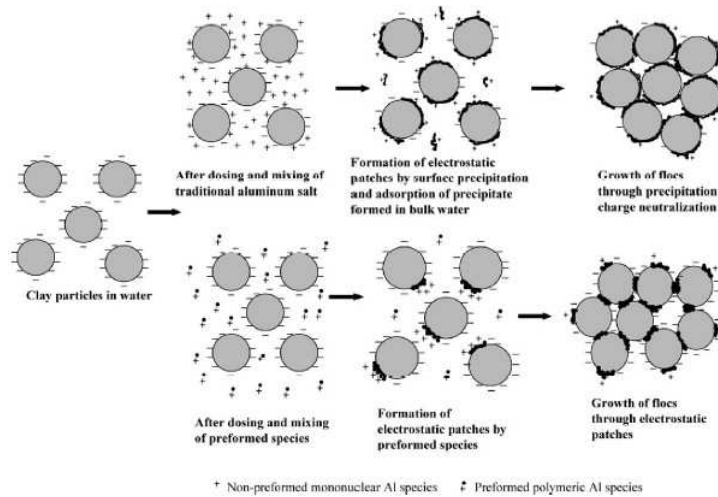


Fig. 2. Schematic diagram of electrostatic patch coagulation.

Figure 1: Schematic diagram of electrostatic patch coagulation

This could be used to explain the mechanism of electrostatic patch coagulation.

1.2 Distinct coagulation mechanism and model between alum and high Al_{13} - PAC[2]

1.2.1 PACl working mechanism

Main mechanisms for PACl are electrostatic patch coagulation and bridge-aggregation while charge neutralization also has some effects on the flocculation process. The residual turbidity declined sharply at very low aluminum concentrations and the lowest occurred far before the isoelectric point but then increased. The corresponding optimum coagulant dosages were 10^{-6} mol/L. We can draw this result from Fig.2

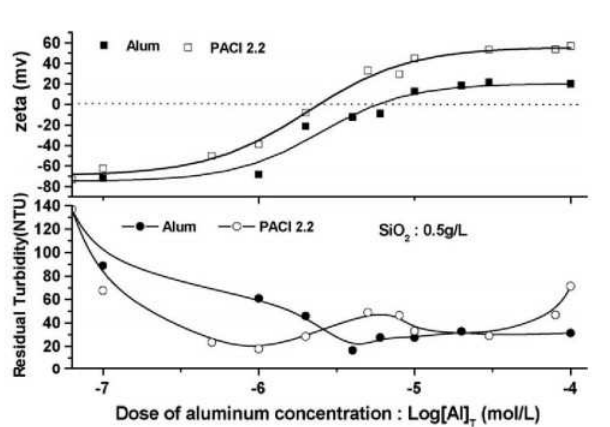


Figure 2: The ξ -potential and residual turbidity curves as a function of aluminum dosage during coagulation of 0.5 g/L silica microsphere suspension by alum and PACl 2.2 (pH 6.5; $NaNO_3$: 0.01M; $NaHCO_3$: 0.001M)

The author thinks that the rapidly adsorbed species may aggregate, rearrange and finally form electrostatic patches over portions of particle surface. The positively charged patches could attract negative silica particle aggregation. As the dose of PACl increased further, re-stabilization appeared after the maximum turbidity removal. The author thinks this implied that particles repelled each other. However, with further addition of PACl, the residual turbidity declined again due to some amorphous precipitates formed giving sweep-flocculation.

This is the detailed information we could use for our hypothesis. Also the re-stabilization should be noted.

1.2.2 Surface coverage and adsorption isotherm models

The results show that the maximum surface coverage of PACl was around 0.4. The optimum coagulation of silica suspension after PACl addition occurred when surface coverage was less than 0.1. The author says it is reasonable to suggest that for PACl, the electrostatic interaction is the main driving forces for the

adsorption process. This opinion could be used to support our experiment and we also could try to make some effort to improve the utilization of surface.

Due to the stoichiometric relationship between coagulant dosage and surface concentration of dispersion (particle concentration), more precise control of dosage of PACl is required for efficient operation.

1.3 Coagulation of silica microspheres with hydrolyzed Al(III) - Significance of Al_{13} and Al_{13} aggregates[3]

1.3.1 Coagulant size distribution and morphology

Colloidal aluminum species formed with increasing basicity. With increasing B values, particle size increases from about 10 to several dozen nm and the large size section becomes broader. We should pay attention to this conclusion because the basicity influences the coagulant size. Also, the author hypothesizes that Al_{13} aggregates were formed by the individual Al_{13} unit via out-sphere bridging and these structures maintain the identical tetrahedral environment under certain conditions.

1.3.2 Zeta-potential of coagulants

Positive zeta values are stable in the pH range of 4-7 for coated silica particles. Since the zeta values of Al_{13} aggregates are higher than the pure Al_{13} in the acidic range, the author assumes that Al_{13} aggregates might release Al_{13} units under pH shock. Here is a relationship between pH and the size of the coagulants.

1.3.3 Floc size distribution

During the experiment, large flocs of $\sim 500\mu m$ are formed at lower dosage. However, without enough positive polycations to destabilize negative silica particles, particle aggregation induced by B2.8 is retarded, resulting in a lower turbidity removal. In this part, we could conclude that if we only pay attention to the get the big size of the PACl, we might fail because we ignore the effect of the positive polycations.

1.4 The effect of total hardness and ionic strength on the coagulation performance and kinetics of aluminum salts to remove humic acid[5]

1.4.1 The effect of ionic strength on removal efficiency

In this study, the removal efficiency of HA and HA-kaolin water decreased with increasing ionic strength for PACl and Nano-PACl. We can draw this conclusion from Fig. 3 and Fig. 4.

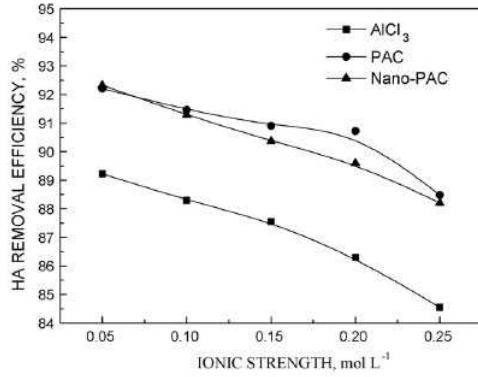


Figure 3: Effect of ionic strength on coagulation performance in HA water treatment.

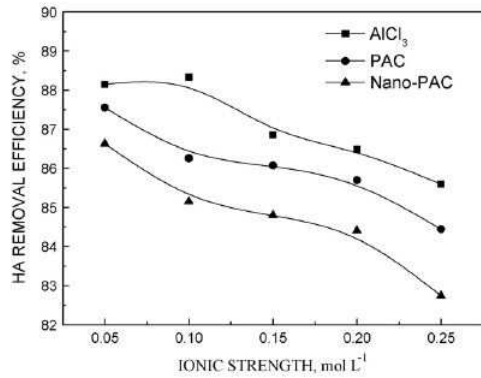


Figure 4: Effect of ionic strength on coagulation performance in HA-kaolin water treatment.

The author thought this is because with increasing ionic strength of water, the activity of PACl's hydrolysis products decreases. We could use this to inform our expected results.

1.4.2 The effect of ionic strength on PACl

As ionic strength only influences the activity of charged ion, for given ionic strength, PACl containing Al_{13} with the highest charge would lose more activity than other aluminum species. As a result, the PACl's removal efficiency is lower than aluminum species (Fig. 3).

1.5 Effect of ionic strength and competitive adsorption of Na^+ on the flocculation of lauryl sulfate micelles with Al^{3+} [7]

1.5.1 Effect of Na^+ on competitive adsorption of cations onto the micellar surfactant

The paper shows the effect of $NaCl$ concentration on the flocculation curves (Fig. 5). An increase in $[NaCl]$ results in an increase in the residual surfactant concentration and a narrowing of the region of optimal flocculation. This is because when Na^+ concentration is much higher than Al^{3+} , Na^+ will have higher possibility to cover most of the micelles, a neutral bonding site where flocculation can occur. This is consistent with the binding factor (β) result in Fig. 6: with increasing in $[NaCl]$, β becomes smaller, which means Al^{3+} is lower, and the neutralization is less effective. As Na^+ is not a powerful coagulant, high concentrations of Na^+ result in poor removal efficiency. The competition of Na^+ delays effective shielding of the micelles by Al^{3+} until higher Al^{3+} is present.

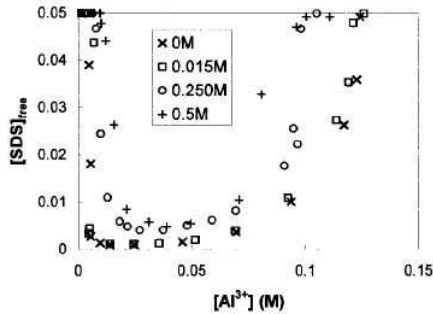


Figure 5: SDS remaining in solution in the presence of a given free Al^{3+} concentration for different overall $[NaCl]$

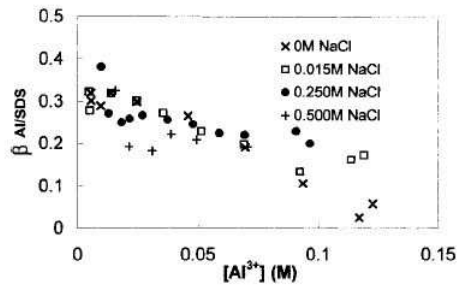


Figure 6: Binding factor (defined as the ratio of Al to SDS ions in the flocculate) vs free Al^{3+} concentration

1.5.2 The effect of ionic strength

In this paper, the author assumes the chemical activity constant above $I = 0.38$ mole/L, so Davies equation $\log \gamma = -0.5z^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right)$ is used here.

From Davies equation we could deduce that, with the addition of $NaCl$, the chemical activity (γ) is reduced. But from the result show in Fig 7, the minimum solubility region loosely corresponds to the higher activities within each series, but the actual values of the activities corresponding to optimum flocculation or full solubility regions are quite different between series. So the author concludes a decrease in the ratio of flocculation is not a matter of the activity of Al^{3+} dropping below a giving critical value to achieve the adequate binding of Al^{3+} on the micelles.

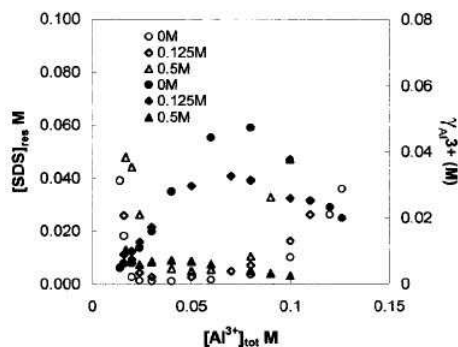


Figure 7: Residual SDS concentration remaining in solution (white symbols) and activities of Al^{3+} (black symbols) against Al^{3+} concentrations.

1.6 Effects of Ca on the distribution, structure and morphology of aluminum species in polyaluminum chloride[8]

1.6.1 Effect of Ca on distribution of Al

The results from this study can be seen in Fig.8 below.

The results show that both Al_m and Al_{13} content increase after $CaCl_2$ is added and Al_{13} is much higher if $CaCl_2$ is added before the basification. This is useful since Al_{13} is the optimal species in PAC for flocculation.

The δ and linewidth in NMR spectra of Al_m and Al_{13} decrease when the Ca/Al molar ratio of the sample rises. The decrease of δ and linewidth implies the structure and chemical environment of Al_m and Al_{13} are changed due to the shielding of the sixfold or fourfold coordinated Al in Al_m or Al_{13} . The ability of PACl to self-aggregate is reduced due to the complex of Ca^{2+} with the oxygen atom of Al species to form the structure of $Al-O-Ca$. This is an explanation for the improved coagulation performance with higher ionic strength since it means the Al species in PAC tend to be smaller after adding $CaCl_2$. Also the Al species becomes scattered and its tendency to polymerization decreases due

to the repulsion between the positive charges on Ca or Al species. This is good for our experiments because we need the relatively small Al aggregates rather than the large ones because the smaller one is more effective and would have high charge neutralization ability.

Ca-adding method	Ca/Al molar ratio	Content of Al species (%)			δ of Al species		
		Al_m	Al_{13}	Al_u	inner reference	Al_{13}	Al_m
No Ca	0	7.76	52.32	39.91	80.12	62.887	0.058
Adding Ca before the basification	0.2	10.11	60.37	29.51	80.12	62.866	0.048
	0.4	10.42	62.26	27.32	80.12	62.845	0.037
	0.6	10.52	59.80	29.67	80.12	62.834	0.037
Adding Ca after the basification	0.2	10.47	67.48	22.05	80.12	62.865	0.047
	0.4	10.24	65.37	24.39	80.12	62.844	0.037
	0.6	10.03	63.41	26.56	80.12	62.834	0.037

Figure 8: Effect of Ca-adding on the content and chemical shift of Al species in PAC

1.6.2 Effect of Ca on structure and morphology of Al species.

The results are shown in the Fig.9. We can see that the Al species tend to scatter and the density of the aggregates decreases with the increasing of Ca/Al molar ratio. The branch aggregates disappear gradually and are converted into granules whose diameter is diminished as function of the Ca/Al ratio. The images support the idea that we could get smaller Al species by adding Ca .

Also, adding Ca could prevent the Al_{13} species aggregated in solution and enhance the charge neutralization ability of PAC and improve its flocculation efficiency in water treatment.

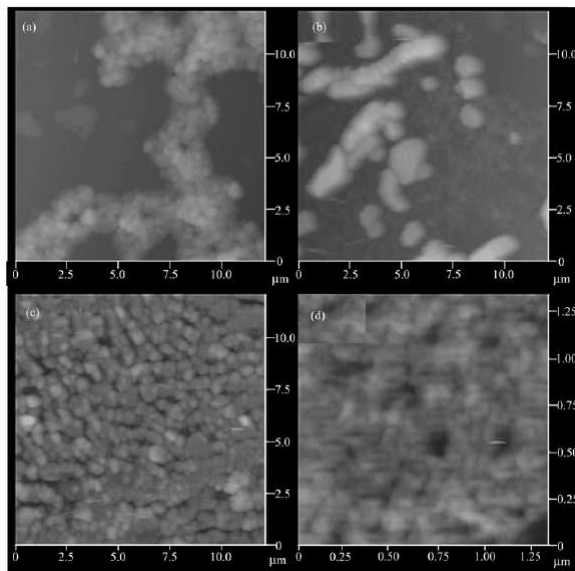


Figure 9: AFM images of PAC with different Ca/Al molar ratio. (a) $Ca/Al=0$; (b) $Ca/Al=0.2$; (c) $Ca/Al=0.4$; (d) $Ca/Al=0.6$.

2 Materials and Methods

2.1 Particle Size Experiment

2.1.1 Particles and coagulants

All chemicals used in this study were of analytical grade except those being specifically mentioned, and solutions were prepared with deionized water.

1. Clay particles

Kaolin clay was used as model particles in this study because of their strong negative charge in suspension, homogeneity and simple morphology. The raw water was prepared by mixing the clay solution with the water in tank.

2. Coagulants

Polyaluminum chloride (PACl) was used as the coagulant in this investigation. We used unfiltered and vacuum filtered coagulant to go through the tube flocculator, and test the RT respectively. Unfiltered coagulant was prepared by dissolving coagulant in deionized water. Vacuum filtered coagulant was prepared with unfiltered coagulant filtered with filter papers with pore size $0.70\mu m$, $0.45\mu m$ and $0.10\mu m$ in turn.

Our hypothesis is that the electrostatic patch is a major mechanism for PACl coagulation. We assume that with a big enough coagulant particle

size, the patches could function efficiently. Because if the patch size was bigger than the optimal size, it was a waste of coagulant as the middle part of the patch did not contribute to successful flocculation; if the patch size was smaller than the optimal size, it was not strong enough to form electrostatic attraction between clay particles and precipitate. So, we try to use the vacuum filtered coagulant to find the optimal size of the coagulant to get a good and efficient coagulation.

2.1.2 Tube Flocculator RT experiments

Coagulation experiments were conducted in a tube flocculator apparatus.

To initiate an experiment, a total amount of 5 mL/s working suspension was transferred to the tube flocculator plant. The suspensions went through several small radius loops in order to get rapidly mixing, and went through a 84m long and big radius loop to get slow mixing. The flocs were allowed to settle for 30 min before residual turbidity measurements were taken. After sedimentation, supernatant samples were withdrawn for pH measurements. The RT and pH measurements were conducted using a turbidimeter (XX, XX, Co., USA) and a pH meter (XX, XX, XX), respectively.

This experiment was investigated to test the RT removal efficiency of the unfiltered and vacuum filtered coagulants.

2.1.3 Coagulant particle size measurement

The coagulant particle size measurement were conducted using a Zetasizer analyzer (Malvern Co., UK).

This experiment was to test the particles size of the vacuum filtered coagulator, and try to figure out the exact particle size after vacuum filtration.

2.1.4 Coagulant absorbance measurement

The coagulant absorbance measurement were conducted using a spectrophotometer (XX,XX , Co., UK). The specific process can be found at Eriochrome Cyanine R Method[6].

Before testing the coagulant absorbance, we first test the absorbance of standard solutions of known concentration, and use the absorbance results to draw a graph which shows the relationship between concentration and absorbance. Then we test the absorbance of the unfiltered and vacuum filtered coagulant. Use the absorbance and find the corresponding concentration to figure out the concentration of the coagulant.

This experiment was investigated to determine the concentration of the coagulant. Because although we knew the concentration of the coagulant, after filtering, the concentration of vacuum filtered coagulant decreased. And in this way, we can figure out the exact concentration of the vacuum coagulant.

2.2 Ionic Strength Test Experiment

2.2.1 Materials

All chemicals used in this study were of analytical grade except those being specifically mentioned, and solutions were prepared with distilled water. The coagulants and the clays are the same as the particle size experiment.

2.2.2 Jar Test 1

The objective of the first jar test is to find the optimal dosage of the Na_2CO_3 which controls the chemical stock concentration when running the tube flocculator apparatus. The Na_2CO_3 is used to control the pH of the water because we need to maintain the pH at 7.5 throughout each experiment. This is a critical process to make sure our final results will be reliable. Firstly, we put 1.152 mg PACl into 1.0 L distilled water and then slowly add the Na_2CO_3 into the mixed water. At the same time, we stir the water to make the chemicals mix well. During the mixing period, pH is monitored using the pH probe. When the pH reaches 7.5, we stop adding Na_2CO_3 and record the concentration. The same processes are repeated to make sure we could get a reliable result. Then we could use a simple equation to calculate the concentration of Na_2CO_3 which we need for the stock solution. Also, through the jar test we found that adding some clay into the water does not change the pH of the distilled water. That means the mixing process of the coagulant and clay does not change the pH. The conductivity of the jar solution is recorded after the pH is adjusted. Then we use the relationship between the conductivity and the ionic strength to calculate the real ionic strength in the whole apparatus.

2.2.3 Jar Test 2

The objective of the second jar test is to find the relationship between the experimental ionic strength and theoretical ionic strength, as these two ionic strengths do not equal in previous experiments. In this test, conductivity is used as the indicator of experimental ionic strength, because experimental ionic strength cannot be got from the conductivity probe directly, and according to the Russell approximation: $I = 1.6 \times 10^{-5} \times \text{Specific Conductance (in mmho/cm)}$, the experimental ionic strength can be estimated from the conductivity. It should be noted that the Russell approximation is only valid when ionic strength is less than $10 \frac{\text{mol}}{\text{m}^3}$.

Firstly, we added PACl (69.3g/L) (refer table 1 for the detailed dosage) into 1.0L distilled water and slowly added the Na_2CO_3 into the mixed water to make the pH approaching 7.5. Then we controlled the amount of clay (refer table 2 for the detailed dosage) added to control the turbidity of raw water. After adding clay, we recorded the pH and conductivity. As previous experiments showed that clay does not influence the conductivity and pH of water. The amount of PACl and Na_2CO_3 added could be used to calculate how much $NaNO_3$ is needed to reach ionic strength to 0.5, 5 and 10 (refer table 3 for the detailed

Target Ionic Strength (<i>mole/m³</i>)	0.4	1	5	10
Influent Turbidity (NTU)	15	50	100	150
Coagulant Dose (mg/L)	1.00	2.01	3.01	4.02

Table 1: Experiment Condition

dosage) using MathCAD. After dosing the $NaNO_3$, we recorded the final pH and conductivity.

2.2.4 Tube Flocculator RT test experiments

In this part, the whole process is the same as the particle size experiment except we use the distilled water instead of the tap water. Also, another stock tank of Na_2CO_3 is needed to maintain the pH at 7.5. During the experiment, we take some water from the output tube to test the conductivity of the treated water.

3 Analysis

3.1 Particle Size Experiment

Currently, we just ran some experiments and there are no final results. This is a description about our theory and expected results.

As electrostatic patch serves an important role in coagulation, we assume that some of the coagulant patches was not utilized efficiently. Because some coagulant in the middle part of the patch did not work actually, and this caused the waste of coagulation. So through filtration, we try to find out the optimal coagulant particle size range when the coagulant can be strong and big enough to form the electrostatic patches or bridges between flocs.

Based on the theory and our hypothesis, our expectation is that the raw water treated by the vacuum filtered coagulant would have a lower residual turbidity compared with unfiltered coagulant.

3.2 Ionic Strength Experiment

Currently, we just ran some experiments and there are no final results. This is a description about our theory and expected results.

As clay particles have a negative charge, and we assume charge neutralization and electrostatic patches are the main mechanisms for clay particles moving from tap water. According to the Debye length calculation equation $\frac{1}{\kappa} = \sqrt{\frac{\epsilon_r \epsilon_0 k_b T}{2N_A e^2 I}} [4]$, when decreasing the ionic strength, the Debye length of the clay particles gets bigger. Thus, the repulsion between clay particles is felt over larger distances. That means with the increasing ionic strength, it is easier for coagulant and clay particles collision and form precipitation.

Based on the theory and our hypothesis, our expectation is that distilled water which has the lowest ionic strength would have a worse turbidity removal efficiency than tap water which has a higher ionic strength.

3.2.1 Relationship between PACl Dosage and Na_2CO_3

From Figure 5, we found that with the increasing of PACl dosage, the needed dosage of Na_2CO_3 to maintain the pH at 7.5 displayed an increasing trend and reached the highest point when PACl dosage equaled to 4.0194gm/L. Based on the theory, there should be a linear relationship between PACl dosage and needed Na_2CO_3 . But in the experiment, when we linearize all scatter points, R^2 is around 0.44-0.81 which indicates a poor fit of the equation, so we cannot conclude the relationship by using the linearize equation.

It should be noticed that we assume clay has little influence on the pH of the system, however, the experiment reveals that raw water's turbidity has some impact on the needed dosage of Na_2CO_3 , especially the turbidity reached 150NTU.

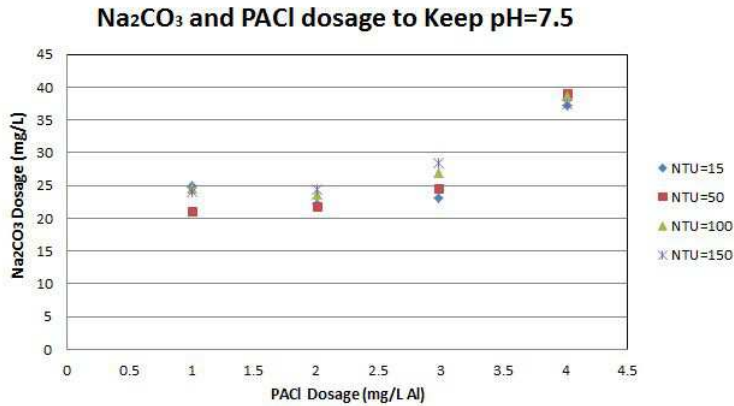


Figure 10: Dosage relationship between PACl and Na_2CO_3 to maintain pH=7.5

3.2.2 Relationship between Ionic Strength and Conductivity

From the Figure 6 and 7, we found a good linear relationship between ionic strength and conductivity. It should be noticed that, when we linearize the scatter plots, the trendlines were forced through zero (y-intercept =0) because we know that if the ionic strength is zero, the conductivity must be zero. The linearization equation could be concluded as: $Ionic\ Strength = 0.0080 \times Conductivity\ (in\ mmho/cm)$, and this equation used to calibrate the relationship between Ionic strength and conductivity has an extremely good fit ($R^2 = 0.99$).

Also, the turbidity and the PACl dosage do not influence the relationship between ionic strength and conductivity.

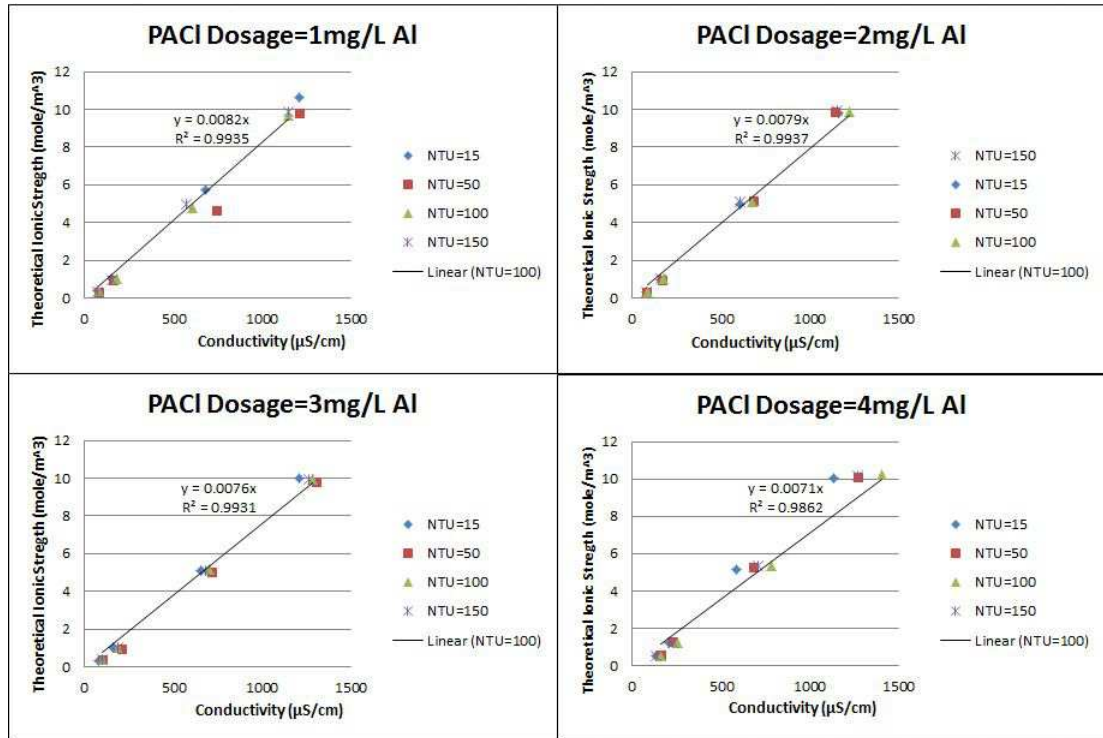


Figure 11: Relationship between ionic strength and conductivity under different turbidities

The linearization equation from the above graph that is : $Ionic\ Strength = 0.0079 \times Conductivity\ (in\ mmho/cm)$

Since the relationship between ionic strength and conductivity is very similar as the turbidity and the PACl dose change, we could use this equation for various turbidities and PACl doses.

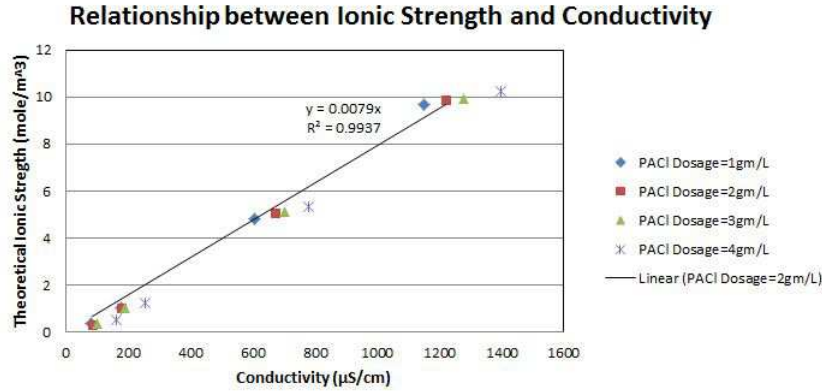


Figure 12: Relationship between ionic strength and conductivity under different PACl dosages when turbidity=100NTU

4 Conclusions

4.0.3 Ionic Strength Experiment

1. Based on our experiments, the relationship between PACl dosage and needed Na_2CO_3 dosage is nonlinear, and high turbidity of raw water would increase the needed dosage of Na_2CO_3 .
2. There is a strong linear relationship between theoretical ionic strength and experimental conductivity. The relationship is approximately $Ionic\ Strength = 0.0079 \times Conductivity$ (in $mmho/cm$).

5 Future work

5.1 Particle Size Experiment

In the future, more information is needed to build a complete hypothesis to explain our experimental results in this area. Future work includes reading papers about PACl that focus on the influence of the coagulant size on turbidity removal efficiency. Moreover, more experimentation is needed under controlled conditions to see if the results are consistent with the hypothesis we made.

5.2 Ionic Strength Experiment

1. Read more literature about ionic strength and continue the research.
2. Experiment further to verify the relationship between needed dosage of Na_2CO_3 and PACl is needed. Since changing the concentration of Na_2CO_3 during the experiment may lead to a big change in the needed dosage of

Na_2CO_3 , we will try to use the same concentration of Na_2CO_3 to finish a set of experiment to minimize the error from the dosage concentration.

3. Find out the particular ions which influence flocculation efficiency over a range of coagulant doses. Because experiments between tap water and distilled water shows that tap water has a wider flocculation range and higher removal efficiency, we want to find out which ions in the tap water are responsible.

References

- [1] Dongsheng Wang, Changqing Ye, Alkalinity effect of coagulation with polyaluminum chlorides: Role of electrostatic patch, Colloids and Surface A: Physicochem. Eng. Aspects. 294 (2007) 163-173.
- [2] Xiaohong Wu, Xiaopeng Ge, Distinct coagulation mechanism and model between alum and high Al13-PACl, Colloids and Surface A: Physicochem. Eng. Aspects. 305 (2007) 86-96.
- [3] Xiaohong Wu, Dongsheng Wang, Coagulation of silica microspheres with hydrolyzed Al(III) - Significance of Al₁₂ and Al₁₃ aggregates, Colloids and Surface A: Physicochem. Eng. Aspects. 330 (2008) 72-79.
- [4] Debye length, http://en.wikipedia.org/wiki/Debye_length. 9(2011).
- [5] Yan Wang, Bao Yu Gao, Xiu Ming Xue, Wei Ying Xu, The effect of total hardness and ionic strength on the coagulation performance and kinetics of aluminum salts to remove humic acid, A: Physicochem. Eng. Aspects. 160(2010)150-156
- [6] Powder Pillows, 2010. Aluminum-Eriochrome Cyanine R Method (Edition 6). U.S.A., Hach Company, 1-9.
- [7] P. Paton-Morales and F. I. Talens-Alesson, Effect of ionic strength and competitive adsorption of Na^+ on the flocculation of lauryl sulfate micelles with Al^{3+} . Langmuir 2001, 17, 6059-6064.
- [8] Zhao Huazhang, Ge Xiaopeng, Luan Zhaokun, Effects of Ca on the distribution, structure and morphology of aluminum species in polyaluminum chloride. Chinese Science Bulletin, 2004 Vol. 49, No. 12 1241-1244.