

# Treatment of Highly Turbid Water by Polyaluminum Ferric Chloride (PAFCL)

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## A-R-T-I-C-L-E-I-N-F-O

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## A-B-S-T-R-A-C-T

**Background & Aims of the Study:** In some situation like rainfall seasons raw water become very turbid so it affected the water treatment plant processes and quality of produced water. Treatment of very high turbid water has some concerns like precursors for disinfection by-products and very loading rate of particle on filter's media and consequently increases in water consumption for filter backwash. This paper investigates the performance of a composite inorganic polymer of aluminium and ferric salt, Polyaluminium ferric chloride (PAFCL), for the removal of turbidity, color and natural organic matter (NOM) from high turbid water.

**Materials and Methods:** Experiments were carried out by Jar test experiment by synthetic water samples with 250 and 500 NTU turbidity that prepared in laboratory.

**Results:** The results of conventional jar test showed that the optimum pH for coagulation of water sample was 7.5 to 8 and optimum dosage of the coagulant was 10 mg/L. Removal efficiency of turbidity, color and UV adsorbent at 254 nm at optimum dose and pH without filtration was 99.92%, 100% and 80.6% respectively for first sample (250 NTU) and 99.95%, 99.49% and 84.77 for second sample (500 NTU) respectively.

**Conclusion:** It concluded that polyaluminium ferric chloride has a very good efficiency for the removal of turbidity, color and organic matter in high turbid water. Also it can be select as a coagulant for high turbid water and some waste water from water treatment plant like filter backwash water.

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## Background

Surface waters usually contain colloidal and dissolved organic substances, such as humic or fulvic acids (1). One of the important physical characteristics of water is Turbidity. It is caused by suspended matter or impurities like clay, silt,

inorganic and organic matter, plankton and other microscopic organisms. Also it is an important operational parameter and indicator in water treatment process. The turbidity levels in the water to be disinfected must be <1.0 NTU. High levels of turbidity can protect microorganisms from the effects of disinfection (2,3). Removing the majority of NOMs and

particulate matter would greatly reduce the load on the filter media in water treatment plant. On the other hand it causes backwash frequency reduction. In drinking water treatment coagulation is a critical process for NOM and turbidity removal. It involving colloid charge neutralization followed by aggregation into flocs that are separated by subsequent processes such as sedimentation or filtration (4,5). Proper and optimum coagulation is essential for good filtration performance and for disinfection byproduct (DBP) control (6-10). The high turbidity in surface water makes it difficult for water treatment plants to supply drinking water (11).

The formation of disinfecting by-products (DBP) which are thought to be carcinogens might result from the chlorination of water with concentration of natural organic matter. The conventional chemical coagulation process is effective in removing colloidal particles and NOMs (12-14). Coagulants used for water and wastewater treatment are predominantly inorganic salts of aluminium and iron. Factors such as the nature of the water, the coagulation pH, kind of coagulant and the dose of coagulant influence the treatment performance (15). Conventional coagulants (inorganic salts of  $Al^{+3}$  or  $Fe^{+3}$ ) are predominantly used for water and wastewater treatment. Today one of the attractive ways for improving the efficiency of coagulation is the use of pre-polymerized coagulants (16-17). These coagulants contain pre-hydrolysed forms of the metals like tridecamer  $Al_{13}$  (18). Superiority of the pre-hydrolysed coagulants as compared with conventional coagulants are including different metal species distribution in the polymerized format, more efficiency in lower dosages range; lower sensitivity to water temperature variation, very low effect on alkalinity consumption in treated water or buffering effect of them in treated water and control their degree of hydrolysis during manufacture, so the complicated reactions caused by the hydrolysis

of the metal salt in coagulation can be reduced (19-23).

In many countries polyaluminum chloride (PACl) is widely used as coagulant in water and wastewater treatment due to its high efficiency at low dosage, low cost and convenient application (24,25). Another newly pre-polymerized coagulant is polyaluminum ferric chloride (PAFCl). Really there aren't any more research about application of this coagulant for high turbid water, so the aim of this study is to find out the optimum coagulation conditions and suitability of PAFCl for the removal turbidity, color, and organic material absorb UV254 in high turbid water and also determination of residual Aluminium ( $Al^{3+}$ ), Iron ( $Fe^{2+}$ ) and some heavy metals in treated water.

## Materials & Methods

### Preparation of turbidity and Water samples:

10 grams of kaolin, heavy grade (BDH Chemicals) was added to 2 liter distilled water. 0.5 kg of river bed soli added to 2 liter of distilled water and mixed for 1 hour. Then after sedimentation about 30 minutes, suspended solution up to sediment added to prepared kaolin solution. Total volume was made up to 4 liter. The suspension was stirred slowly at 30 rpm for 24 hours for hydration of the particles and uniform dispersion (26). Then the stock solution was used in the preparation of turbid samples of water with turbidity of 250 and 500 NTU. The adjustment of pH was conducted with 0.1 M  $H_2SO_4$  and 0.1 M NaOH solution. For optimal pH selection, constant dose of PAFC (8 mg/L) was added to sample and jar test conducted at various pH. The best output in cording to maximum removal selected as optimum pH. Of course latest study showed that best pH for PAFC performance was 7 to 8. Based on optimal pH, selection of optimal polyaluminium ferric chloride dose was carried out. Table 1 shows the characteristics of the samples.

### Experimental procedure

The Jar test principle including coagulation, flocculation and settlement were conducted for this study. Coagulation was carried out by simultaneous use of 6 beakers with 1000 ml in volume; each equipped with an rpm adjustable agitator. The adopted experimental condition include coagulation with rapid mixing at 120 rpm for 2 min, flocculation with slow mixing at 40 rpm for 10 min and settlement by a settling period of 20 min. Samples of the treated water were collected at a depth of 2.5 cm below the supernatant surface. To attain an optimal pH, a constant dose of PAFCl (8 mg/L) was used for the coagulation process at various pH (5 to 11). Optimal pH was adopted as the pH which leads to gain the best results for turbidity and color removal. Applying the identical optimal pH with different doses of PAFCl, its optimal dose of application was selected. Thus the coagulation procedure was conducted for two turbid water samples according to the optimal pH and dose.

#### Analytical methods

Samples were analyzed before and after coagulation for residual turbidity, true color, UV254 absorbance, residual aluminium (Al), iron (Fe), and heavy metals like arsenic, lead, nickel and chromium. All examination was conducted according to standard method for examination of water and wastewater (27). Turbidity, color, TDS, EC and pH of the samples were measured by TN-100(EUTECH) Turbidimeter, DR 5000- HACH LANGE, EC meter SENSION5 (HACH LANGE) and pH-meter model CG 824, respectively. For true color analysis, treated water was already filtered using a 0.45- $\mu$ m filter.

#### Preparation of coagulant solution

The PAFCl coagulant commercial grade product with a composition of 28% as  $Al_2O_3$ , 1.84% as  $Fe_2O_3$  and basicity of about 81.22% was purchased from a Chinese company. Its molecular formula was:  $[Al_2(OH)_nCl_{6-n}]_m [Fe_2(OH)_nCl_{6-n}]_m (SO_4)_x$ . For preparation of the coagulant stock solution, 1 gr of PAFCl was

solute in to 1 liter distilled water to achieve a concentration of 1 mg/L.

## Results

The characteristics of turbid water samples are reported in Table 1.

Table 1) quality of samples be for coagulation with PAFCl

Parameter	Sample 1	Sample 2
Turbidity (NTU)	250	500
Color (Pt.Co)	157	198
EC ( $\mu$ s/cm)	349	425
TDS (mg/L)	175	224
pH	7.8	7.8
Alkalinity (mg/L)	132	136
Temperature 0C	23	23
Sludge volume	0.5	1.5
UVA-254nm (cm-1)	0.134	0.197
DOC ( mg/L)	0.8	0.92

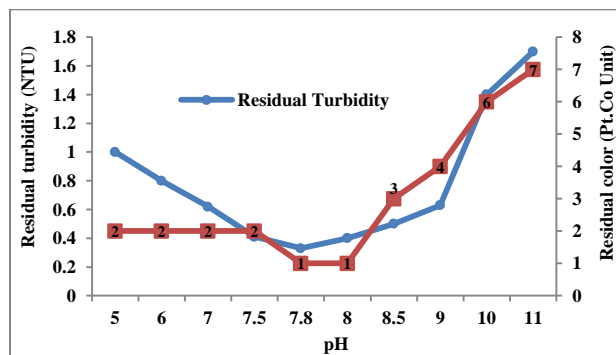


Figure 1) Optimum pH for turbidity and color removal by 8 mg/L PAFCl (initial turbidity and color was 250 NTU and 157 Pt.Co Unit respectively)

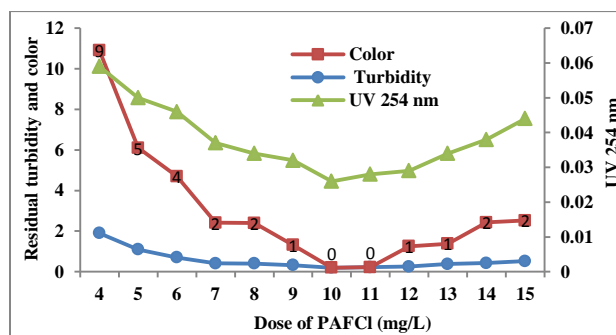


Figure 2) Optimum PAFCl dose selection based on pH 7.8 with initial turbidity 250 NTU, color of 157 Pt.Co Unit and UV<sub>254</sub> absorbance 0.134 nm

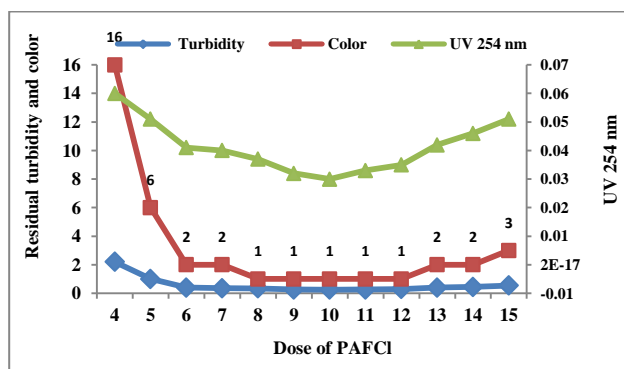


Figure 3) Optimum PAFCI dose selection based on pH 7.8 with initial turbidity 500 NTU, color of 198 Pt.Co Unit and UV254 absorbance 0.197 nm

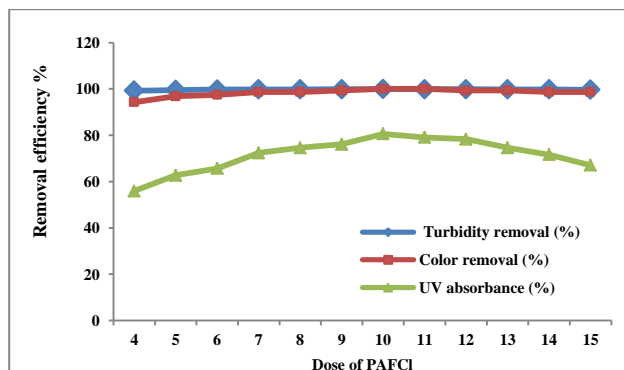


Figure 4) Removal efficiency of turbidity, color and UV adsorption for first sample at various dose of PAFCI

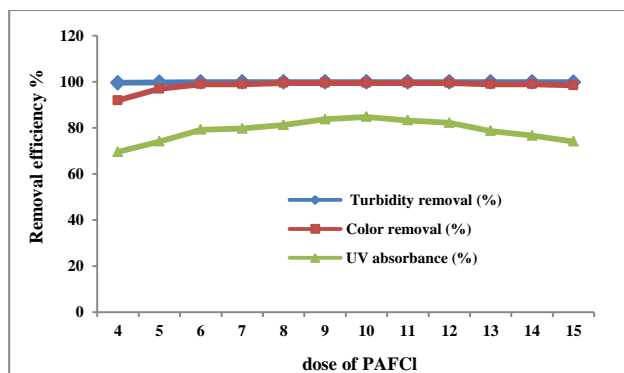


Figure 5) Removal efficiency of turbidity, color and UV adsorption for second sample at various dose of PAFCI

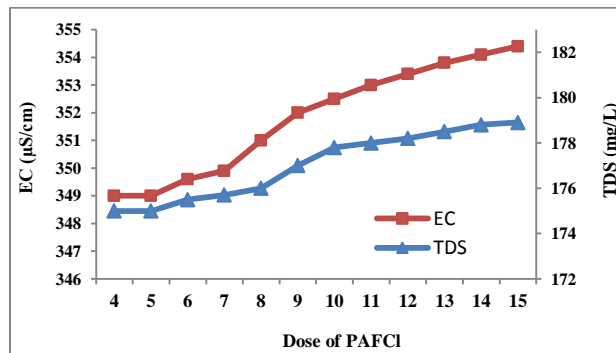


Figure 6) The variation of TDS and EC value after coagulation by PAFCI with different dose, (Primary TDS and EC were 175 mg/L and 349 µS/cm respectively)

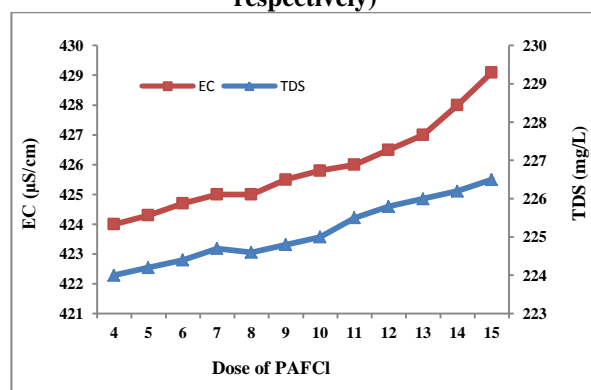


Figure 7) The variation of TDS and EC value after coagulation by PAFCI with different dose, (Primary TDS and EC were 224 mg/L and 425 µS/cm respectively)

Table 2) The concentration of heavy metals and amounts of UVA<sub>254</sub> nm and SUVA before and after coagulation

Heavy metals	Sample 1		Sample 2	
	C.B.Co*	C.A.Co**	C.B.Co*	C.A.Co**
Al (µg/L)	27	35	45	51
As (µg/L)	1.6	1.6	1.9	1.91
Cd (µg/L)	0.066	0.066	0.074	0.074
Co (µg/L)	1.9	1.9	2.2	2.2
Cr (µg/L)	17	11	21	14
Cu (µg/L)	88	30	103	62
Fe (µg/L)	254	114	303	184
Ni (µg/L)	0.55	0.56	0.71	0.73
Pb (µg/L)	21	8	33	16
UVA-254nm (cm <sup>-1</sup> )	0.134	0.026	0.197	0.03
SUVA***	1.1	3.25	1.3	3.52

\* Concentration before coagulation.

\*\* Concentration after coagulation.

\*\*\*  $SUVA = \frac{(uv\ 254\ in\ \frac{1}{cm})100}{DOC\ in\ mg/l}$

## Discussion

### Optimum pH selection

pH change have a significant effect on coagulation (28,29). Fig. 1 shows the effect of pH on the PAFCl performance at constant dose of 8 mg/L for turbidity and color removal. Results showed that in the pH value upper than 9 the performance of the coagulant was dramatically decreased. Good efficiency was achieved at pH range from 7 to 8.5 to obtaining residual turbidities  $\leq 0.6$  NTU. However at pH 7.8 the efficiency reached to its optimum which was capable to reduce the turbidity down to 0.33 NTU.

Efficient coagulation of water occurs only within a specific pH range. At the pH value in the range of 7.0 to 8.4, high-polymerized species of PAFCl could effectively make particles to destabilize by charge-neutralization and adsorption-bridge function, so an excellent coagulation performance can be achieved. In contrast, when pH value is higher than 8.4 PAFCl will be hydrolyzed into negatively charged precipitates. Therefore the removal efficiency of turbidity is decreased with increasing of the pH value (30). In acidic water minerals have a high solubility, so in this situation water has a low color. Optimum removal of color was happened at pH 7.8 to 8. At this pH, color removal efficiency was 99.36%. It can be seen that  $\text{pH} \geq 8.5$  decrease color removal efficiency and pH 5 to 8 has a constant effect for color removal (Fig.1). In this study optimum pH was selected as 7.5 to 8 (exact 7.8). Jr-Lin and et al showed that that the optimum pH for PACl-1 coagulation occurred around pH 7, which implies that sweep flocculation (enmeshment) by  $\text{Al}(\text{OH})_3$  was probably the principal coagulation mechanism of PACl (31).

### Optimum dose selection for removal of turbidity, color and UV254

The amount of turbidity and color removal with UV254 absorbance by various doses of

coagulant can be seen in Fig.2 to Fig.5. For two samples by increasing the coagulant dose up to 14 mg/L, the removal efficiency for turbidity, color and  $\text{UV}_{254\text{nm}}$  was increased. Dosage higher than that has worsened the removal efficiency. Maybe re-stabilizing of the colloidal suspension is responsible for this phenomenon. In this study optimum PAFCl dosage of 10 mg/L at pH 7.8 was applied for the set of experiments. By increasing the coagulant concentration the efficiency of turbidity removal was slightly decreased. This may be attributed to charge reversal and destabilization of colloidal particles due to coagulant overdosing (32,33). Also at low dose, the flock did not formed because the coagulant was not adequate to compress the double layer of the colloid particles or to bind the colloid particles to form bridging.

PAFCl is a positively charged coagulant, so it can effectively remove negatively charged colors from waters by charge neutralization. On the other hand, PAFCl is an inorganic polymer and can aggregate the destabilized dyes together by adsorption-bridge function of the coagulant (30). Results showed that PAFCl have very good efficiency for removal of turbidity and color, producing water with residual turbidity about 0.2 and 0.25 NTU for tow sample respectively. This reduces concerns related to  $\text{turbidity} \geq 1$  NTU which affects the maintenance and operation of water filters. Turbidity is not a direct indicator of health risk but many studies show a strong relationship between removal of turbidity and reduction of protozoa in treated water (33,34). For sample one with initial turbidity and color of 250 NTU and 157 Pt.Co, the removal efficiency in optimum dose of 10 mg/l was 99.92% and 100% respectively (Fig.4). Also for second sample with initial turbidity and color of 500 NTU and 198 Pt.Co, the removal efficiency in optimum dose of 10 mg/l was 99.95% and 99.45% respectively (Fig.5). In fact Because of the increase of turbidity, the collision between particles during the coagulation process will

increase. So increase of collision efficiency will improve the particle-aggregation induced by charge neutralization or electrostatic patch.

### **Effect of coagulation on treated water alkalinity, EC and TDS**

Usually Inorganic coagulants decrease the alkalinity of water so the pH of the chemically dosed raw water will decrease. This often means that supplemental alkalinity in the form of lime; soda ash, or caustic soda will have to be added to maintain an acceptable dosed-water pH. Pre-polymerized coagulants have less impact than conventional coagulants on alkalinity reduction (35). Pre-hydrolysed materials are often found to be considerably more effective because they are already partially neutralized so they have a smaller effect on the pH of water and finally reduce the need for pH correction. Basicity is an important property for polymeric coagulants. This is the ratio of hydroxyl to aluminium ions in the hydrated complex. The low basicity causes the consumption of alkalinity in the treatment process and hence affects pH. In this study our coagulant had 81% basicity. Initial pH and alkalinity of first sample was 7.8 and 132 mg/L. After coagulation at optimum dose and pH, low change in pH and alkalinity occurred amounting 7.7 and 124 mg/L (36). For second sample with initial pH and alkalinity of 7.8 and 136 mg/L low change in pH and alkalinity occurred after coagulation at optimum dose and pH. This parameter reached to 7.7 and 126 mg/L. However, by increasing coagulant dosage pH and alkalinity were slightly decreased but it was negligible. One reason for this phenomenon may be related with this matter that as PAFC hydrolyzation takes place, the flock formed incorporates the chloride ion into the flock's structure so it is not available for producing acid. Usually inorganic coagulants increase the total dissolved solids concentration of the treated water. This action is not very good, especially when using conventional coagulant, anions and cations levels in the finished water will increase.

Chemicals like polyaluminum chloride and polyaluminum hydroxychloride could result in a smaller or even negligible increase in TDS and smaller (or none) need for neutralization (37). Fig. 6 and 7 shows the effect of increasing coagulant dose versus TDS and EC content of treated water. It can be found that PAFCl has very low effect for increasing TDS and EC content of treated water.

### **Sludge production**

Almost all chemical processes of coagulation produce sludge in the form of the metal hydroxide with the colored and colloidal matter that is removed from the raw water.. Polyaluminum chloride produces less sludge than alum when dosed at equivalent levels. In our study, the sludge volume of two samples before coagulation was 0.5 and 1.5 ml/L. The experiments on sludge volume were performed using Imhoff cones. After coagulation with PAFCl at optimum dose, 6.5 and 11 ml/L sludge was produced for two samples respectively. With increasing in coagulant dose we had more production of sludge. Visual observation revealed that flock forming was larger at higher pH value than those at optimum pH conditions. Maybe it related to solubility of Aluminum and Ferric hydroxides in lower pH.

### **Residual metals**

The residual concentration of Al and Fe in treated water is an important subject for application of coagulant. Some coagulant increase heavy metals concentration in treated water so analysis of heavy metals repellence after coagulation is very important. Use of Al-based coagulants especially  $Al_2(SO_4)_3$  (alum) often leads to an increase Al concentrations in treated water. The maximum recommended range of aluminium in drinking water by WHO is 0.05-0.2 mg/L. Table 2 show the specification of treated water quality. It can be seen that PAFCl has not released any heavy metals to treated water. Also in some cases it reduced heavy metals concentration. In this study results showed that the concentration of Fe in treated water was decreased, only Al

concentration was increased about 0.008 and 6 mg/L in first and second sample respectively. A possible explanation of this is that the residual aluminium is low in neutral pH due to the formation of  $\text{Al}(\text{OH})_3$  amorphous precipitates which is then removed by sedimentation. So, residual aluminium drops significantly around neutral pH. Previous study showed that in  $\text{pH} > 7.5$ , due to the formation of soluble  $\text{Al}(\text{OH})_4$ , the residual aluminium content increases in the solution (38). Fe concentration in first and second sample was 0.254 and 0.303 mg/L and after coagulation reached to 0.114 and 0.184 mg/L. Maybe raw water contained mineral-organic combined form of iron; furthermore our coagulant created insoluble aluminum hydroxides produced flakes and absorbed iron compounds (39). PAFCl similar to polyaluminum chloride and polyaluminium silicate chloride leaves low residual Al in treated water (40). Fortunately this coagulant has not repelled any heavy metals (Table 2) like nickel, arsenic; lead and chromium to treated water (41)

#### UV245 and specific UV absorbance

In most water treatment plants, coagulant dosing is controlled by the raw water turbidity and color. It has been suggested that the raw water specific UV absorbance (SUVA) can be used to control coagulation. For water with SUVA of  $\geq 4$  or greater, the natural organic matters (NOM) composition is dominated by humic substance and NOM control coagulant dosing. For water with SUVA between 2 and 4, the water contains a mixture of humic and non humic substances; in this case the NOM can control coagulant dosing. For water with  $\text{SUVA} \leq 2$ , the NOM composition is dominated by non humic substance so the NOM does not control coagulant dosing (42).

The amounts of SUVA in first and second sample before coagulation were 1.1 and 1.3. Also after coagulation it was 3.25 and 3.52 (Table 2).

Two important mechanisms for removal of natural organic matter from solution are precipitation of metal-humic complexes and adsorption of humic substances onto metal hydroxide precipitates. These mechanisms are dependent on the pH and coagulant dose. Adsorption of humics onto metal hydroxide precipitates is dominant at higher coagulant doses and higher pH conditions while precipitation of metal-humic complexes is the dominant mechanism at lower coagulant doses and lower pH conditions (42). Other study showed that when the water contains high organic matter, efficient coagulation depends upon enmeshment by amorphous aluminium hydroxide (31). Reduction in the level of NOM before disinfection minimizes the formation of the disinfection by-products and reduces the disinfectant residual that is required to control the bacteria regrowth in the distribution systems. This contributes to the improvement of water quality delivered to the consumers (43-45).

#### Conclusion

It is founded that optimum pH and dose of PAFCl for treatment of water with turbidity of 250 to 500 NTU was 7.5 to 8 and 10 mg/L respectively. Removal efficiency of PAFCl affected very little at pH range 6 to 9. At this pH range residual turbidity was below 1 NTU. Also Variation in TDS and EC were negligible as the coagulants concentrations were increased. Optimizing coagulation conditions can enhance the quality and quantity of other treatment process. So, PAFCl by high efficiency for removal of color, turbidity and organic matter can improve productivity of water treatment plant and reduce cost of operation and maintenance.

The residual of Al, Fe and other heavy metals concentration after coagulation with PAFCl was much less than the level that have a very bad effect on health. Although PAFCl have

good efficiency for organic material removal but further researches may need to be done to clarify the risk of the disinfection by products after chlorination with this coagulant.

## Footnotes

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### Conflict of Interest:

The authors declared no conflict of interest.

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