

original article

Comparison study of turbidity removal using synthesized poly-aluminum chloride-sulfate and poly-aluminum chloride in aqueous solutions

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ABSTRACT

Aims: In this study, the turbidity removal efficiencies of poly-aluminum chloride (PACl) and poly-aluminum chloride-sulfate (PACs) as a coagulant in aqueous solutions were compared.

Materials and Methods: PACs and PACl were prepared at experimental conditions. A conventional jar test apparatus was used for coagulation experiments. Effects of different conditions such as pH (2-12), coagulant doses of PACl (0.01-1.5 mmol/L as Al) and PACs (0.01-1.8 mmol/L as Al), settling time (0-90 min), initial turbidity (7-575 NTU) on the turbidity removal efficiency were investigated.

Results: The experimental results indicated that the optimum pH during the turbidity removal was 6.5 and 9.5 for PACl and PACs, respectively. The optimum coagulant dosages of PACl and PACs were achieved 0.1 and 1.22 mmol/L as Al respectively. Under these optimal conditions, the turbidity removal efficiencies of 97.85% and 95.85% were observed for PACs and PACl, respectively. Furthermore, the effects of settling time and initial turbidity on turbidity removal efficiency were investigated. The results revealed that the turbidity removal efficiency for the PACs was slightly higher than that for PACl at the same conditions.

Conclusion: PACs as a coagulant improved turbidity removal efficiency compared to PACl. PACs as a coagulant can be used for drinking water treatment. However, the dosage of PACl in comparison with PACs was lower for a similar turbidity levels. Therefore, using of PACs in comparison with PACl must be evaluated economically.

Key words: Coagulation, flocculation, poly-aluminum chloride-sulfate, poly-aluminum chloride, turbidity removal

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INTRODUCTION

Water from a natural source usually contains many dissolved and suspended solids.^[1] Because water pollution has become a worldwide problem, many countries suffered from lack of quantity of high quality and or safe source water.^[2] As,

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suspended particles at the lower end of the size spectrum, colloidal particles, do not readily settle they can be removed by sedimentation and filtration only after physical and chemical conditioning, which is known as coagulation.^[1] Coagulation/flocculation is one of the main processes to remove the colloidal particles.^[3-5] In this process, the physical or chemical properties of colloidal or suspended particles are altered and agglomeration is enhanced to extent that these solids^[6] will be removed by subsequent processes, such as sedimentation, flotation, and filtration.^[7,8] It is evident that coagulation will lower the pollution load and could produce a suitable water recovery.^[9]

Coagulants are one of the key elements in the coagulation process.^[10,11] Coagulation efficiency not only depends on the characteristics of coagulants, but also on the certain water quality parameters, such as pH, total hardness, and ionic strength.^[12]

Conventional chemicals used for coagulation are mostly aluminum and ferric salts^[13,14] that are efficient in forming huge flocs, which can be separated ultimately by sedimentation and filtration.^[15] These coagulants when are added into the water, Al/Fe(III) ions will hydrolyze rapidly in an uncontrolled manner to form a range of metal hydrolysis species, which play an significant role in coagulation and following flocculation performance.^[16] Chemical aspects of coagulation demonstrated that the hydrolysis products are the main active species responsible for charge neutralization and aggregation in particle removal.^[15]

Many coagulation models, mainly for traditional alum, have been proposed. These generally describe the mechanism as a sequence of physicochemical reactions,^[14] charge neutralization, sweep coagulation,^[17] double layer compression and bridge aggregation.^[15]

An effective and important method of improving the efficacy of inorganic Al/Fe(III) coagulants is to partly hydrolyse the Al/Fe(III) salts before their addition to the raw water. These hydrolyzed salts preform optimal polymeric Al/Fe(III) species that act as real coagulants.^[18] The resulting advantages of the pre-polymerized Al/Fe(III) coagulants are the wider working pH range, lower sensitivity to low water temperatures, the lower dose required to achieve an equivalent treatment efficiency, and lower residual metal-ion concentrations.^[16,18] So to increase the efficiency of Al/Fe(III) coagulants in water and wastewater treatment processes, preformed inorganic coagulants have been established.^[18]

Poly-aluminum chloride (PACl) is an inorganic polymer flocculants that has been industrialized quickly and applied broadly for treatment of water and wastewater.^[19]

Poly-aluminum chloride-sulfate (PACS) also is a new pre-polymerized Al(III) coagulant, which was developed based on poly-aluminum chloride (PACl). It produces larger polymeric

species than PACl, which improves the aggregation of particles in water.^[16] On the other hand, PACS and its activities lead it to be more effective in coagulation in some cases.^[14]

Gao *et al.* showed that the particle size distribution of PACS was highly dependent on the $\text{SO}_4^{2-}/\text{Al}^{3+}/\text{SO}_4^{2-}$ molar ratio and the γ value,^[16] basicities ($\gamma = [\text{OH}^-]/[\text{Al}]$).^[2,13,18] It was shown that at a fixed optimal γ value of 2.0, the average size of PACS increased with increasing $\text{SO}_4^{2-}/\text{Al}^{3+}$ molar ratio. On the other hand, the average size of PACS with $\text{SO}_4^{2-}/\text{Al}^{3+} = 0.0664$ was increased with increasing γ value in the range of 0-2.3.^[16]

Yang *et al.* evaluated that PACl comparing to $\text{Al}_2(\text{SO}_4)_3$ had superior coagulation performance in most cases.^[6]

The aim of this study was to compare the turbidity removal efficiency of PACl and PACS as a new coagulant according to optimal dose, optimal pH, and settling time. The effects of initial turbidity on coagulation process were also compared.

MATERIALS AND METHODS

All materials and reagents used in this study were purchased from Merck Company (Merck KGaA, Frankfurter Str., 250 64293 Darmstadt Germany) and had analytical grade. Deionized water was used to make all solutions. Each coagulant preparing procedure is as follows:

Poly-aluminum chloride (PACl) was prepared by adding 14 g Na_2CO_3 slowly into AlCl_3 solution (0.84 mol/L) under intense agitation. The solution temperature was kept at 70°C. PACS also was produced using the pre-determined amount of Na_2CO_3 , which was slowly added to a solution of AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$ (~6.75% Al and optimum molar $\text{SO}_4^{2-}/\text{Al}^{3+}$ ratio of 0.0664) while stirring at room temperature to obtain the desired γ value 2. Then, the mixture was stirred until no bubbles formed and the solution became transparent. This solution was kept for more than 24 h in a refrigerator before use. The specific gravity of prepared PACS was 1.176 g/L in room temperature. All the synthesized coagulants were diluted to a concentration of 1 g/L Al before used as coagulants for the removal of turbidity.^[16]

To prepare, appropriate turbid water few grams of Kaolin (Sigma-Aldrich Co.: Sigma-Aldrich Chemie GmbH, Export Department, Eschenstrasse 5, 82024 Taufkirchen, Germany) were weighted and then were kept in the oven for 2 h at 105°C to be dried. Then, it was taken out to be placed in desiccator to be cooled for several minutes. It was added to a few milliliters of distilled water and then diluted to 2 L with distilled water. At the same time, a stirrer was used to uniform dispersion of kaolin particle preparation for 1 h. To allow complete hydration of the kaolin the mixture was permitted to stand for several hours. After that, the supernatant was withdrawn and kept as stock solution.

A conventional jar test apparatus (Model 7790-402) was used for coagulation experiments. First, one liter of the synthetic test water was transferred into each of the 1.0 L plexi-glass beakers and a six-paddled stirrer was used for mixing. Initial turbidity was 7 ± 0.5 NTU, for all solutions. The turbidity analysis was implemented by a EUTECH Turbidimeter model TN-100: (Eutech Instruments Pte Ltd, Oakton Instruments).

The synthetic test water was stirred rapidly at 150 ± 2 rpm for 2 min during coagulant addition, followed by slow stirring at 40 ± 2 rpm for 15 min. The flocs were allowed to settle for 30 min, and the supernatant sample was withdrawn by a pipet from about 2 cm below the water surface for analysis. The results were the average values from 2 to 3 replicated jar tests and 3 to 5 replicated measurements of turbidity. The coagulation pH was achieved and maintained by the addition of HCl or NaOH for pH solution simultaneously with the coagulant. All experiments were done at environment laboratory temperature (25°C).

To determine, a narrower range of initial pH and coagulant dosage for both coagulants prior to planning the trial runs, experiments were carried out by changing a single factor while keeping all other factors fixed at a specific set of conditions. For this purpose, the behavior of turbidity removal after coagulation was studied under various initial pH ranging between 2 and 12, while the dosages of coagulants (0.37 mmol/L as Al for PACl and 0.74 mmol/L as Al for PACS) were preserved constant. After that, to determine the optimum dosage of coagulants for turbidity removal at optimum pH, different amounts of each coagulant (ranging between 0.7 and 1.41 mmol/L as Al for PACS and 0.01-1.11 mmol/L as Al for PACl) were dosed into the solutions.

To determine, the effects of initial turbidity on the turbidity removal efficiency of studied coagulants, the turbidity of

test water solution was adjusted to 7, 35, 50, 150, 230, 350, and 570 NTU by stock kaolin solution at pH of 6.5, and 9.5 and dosage of 0.1, and 1.22 mmol/L as Al for PACl and PACS were applied, respectively. In all coagulation processes the solution temperature was held constant and at room temperature.

The operation of batch system was carried out for each desired concentration in triplicate and the average of the results was considered.

RESULTS

The influence of different pH on turbidity removal efficiency was investigated at a turbidity of 7 NTU and the coagulant dosage of 0.1, and 1.22 mmol/L as Al for PACl and PACS, respectively [Figure 1]. As can be seen in this figure, initial pH had an important effect on the coagulation behavior of the two Al-based coagulants.

Turbidity removal efficiencies with either studied coagulant increased significantly first with the increase of pH and then decreased slightly when the solution pH was increased.

As shown in Figure 2, turbidity removal efficiency of both coagulants first increased significantly with the increase of coagulant dosage and then decreased slightly when the coagulant dosage was higher than 0.1 and 1.22 mmol/L as Al for PACl and PACS, respectively. In this stage of study, the initial pH of the water solutions was adjusted to optimum pH for both coagulants.

Figure 3 shows, the effect of settling time on the turbidity removal for PACS and PACl, respectively. The settling time for the flocs formed in half of the solution height in the jar

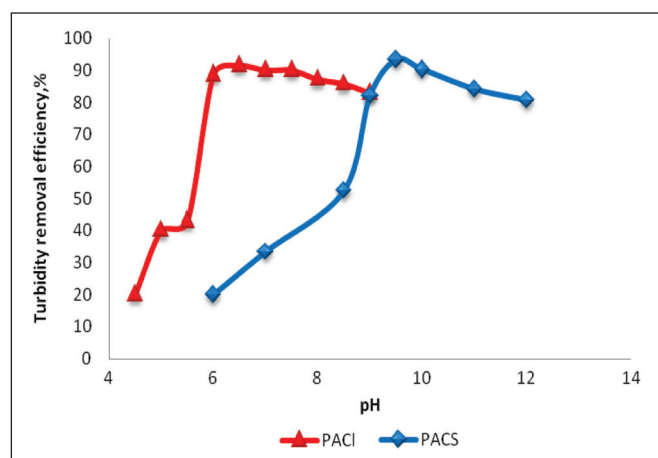


Figure 1: Effect of pH on coagulation performance of poly-aluminum chloride-sulfate and poly-aluminum chloride at dosage of 1.22, and 0.1 mmol/L as Al respectively and turbidity of 7 NTU

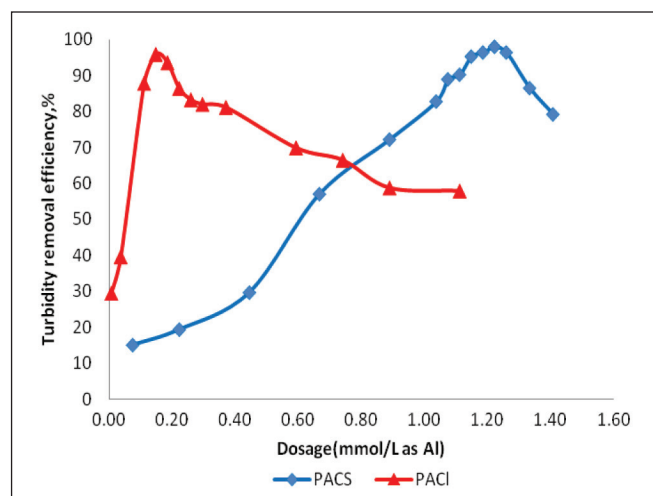


Figure 2: Coagulation performance of poly-aluminum chloride-sulfate and poly-aluminum chloride with different coagulant dosages at the pH of 9.5 and 6.5, respectively, and turbidity of 7 NTU

tests apparatus was recorded. As seen on these figures most particles were removed in the first 5 min, for PACS and PACl.

Figure 4 shows, turbidity removal efficiency of PACl and PACS at different turbidity levels. Both PACS and PACl showed almost the same turbidity removal efficiency patterns for various initial turbidity levels.

DISCUSSION

As indicated in Figure 1, turbidity removal efficiency, for PACS was increased significantly with the increasing of pH in the range of 6-9.5. On the other hand, when the pH was higher than about 9.5, the turbidity removal efficiency was decreased. Thus, the selected optimum pH of PACS as a coagulant for turbidity removal was 9.5. Furthermore, Figure 1 shows the turbidity removal efficiency was increased obviously with pH when initial pH was lower than 7.0 for PACl. While the initial pH was between 7.0 and 9.0, the turbidity removal efficiency decreased insignificantly for PACl. Therefore, the optimum pH of PACl as a coagulant for turbidity removal was 6.5. The effect of pH on turbidity removal efficiency for PACl is related to the formation of high polymeric positive hydrolyzates and $Al(OH)_3$ in the solution in pH between 6.0 and 8.0.^[16] But the effect of pH on the turbidity removal efficiency for PACS can be attributed to the positive aluminum hydrolysis products, which can destabilize negatively charged colloids by charge neutralization.^[16]

As shown in Figure 2, the coagulants dosage had a great effect on their removal efficiency upon turbidity. Generally, low dosages of coagulants are not effective in turbidity removal; however, higher coagulant dosages provide charge neutralization. Thus the flocculation process is done rapid enough to provide settleable flocs. A stable suspension is produced by the increasing coagulant dosages

and reversing the particle charges. A substantial quantity of metal hydrolysis species is produced when further increase is occurred in coagulant dosages. These metal hydrolysis species enmesh positively charged particles in settleable sweep flocs. Therefore, the flocs formed with high coagulants dosages consisted of positive charge.^[20] However, in the case of Al-based coagulants, understanding the distribution of various Al species and the properties of the hydrolyzed Al formed during coagulation is necessary. In the case of PACS, the higher removals might be due to the sweep flocculation mechanism, which is inclined to occur at high PACS dosages.^[19] In the present study, the optimum dosage of PACl and PACS as a coagulant for turbidity removal was obtained to be 0.1, and 1.22 mmol/L as Al, respectively.

Figure 3 shows that both the tested PACS and PACl had the same turbidity removal efficiency-time curve pattern. The turbidity removal efficiency for the PACS was slightly higher than those for PACl at the same time. This can be attributed to the SO_4^{2-} ions in poly-aluminum salts that encourage the aggregation of the hydrolyzed aluminum species. Thus, the formation of larger size polymer species occur and aggregating efficiency may enhance. Therefore, flocs formed by PACS compared to PACl will settle readily.^[16]

In this study, the influence of initial turbidity on the turbidity removal efficiency was studied [Figure 4]. As can be shown in the figure, with the increase of turbidity from 7 NTU to 35 NTU, removal efficiency of turbidity first increased and then decreased when the turbidity reached higher than 35 NTU. Ultimately with the increase of turbidity higher than 250 NTU, removal efficiency of turbidity was increased. Based on these results, it is likely that in the case of low turbidity (7 NTU) due to leakage of colloids formed in suspension even though the surface charges are neutralized, flocs are small with poor settling ability, which increased the residual turbidity and eventually

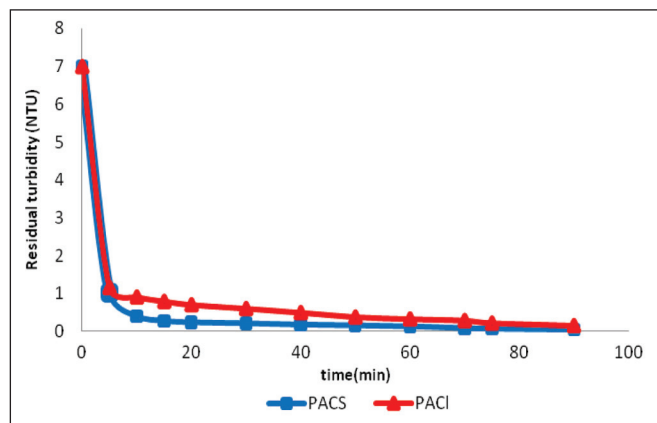


Figure 3: Effect of settling time on the turbidity removal of poly-aluminum chloride-sulfate and poly-aluminum chloride at pH of 9.5, 6.5 and the dosage of 1.22, 0.1 mmol/L as Al respectively and turbidity 7 NTU as Al

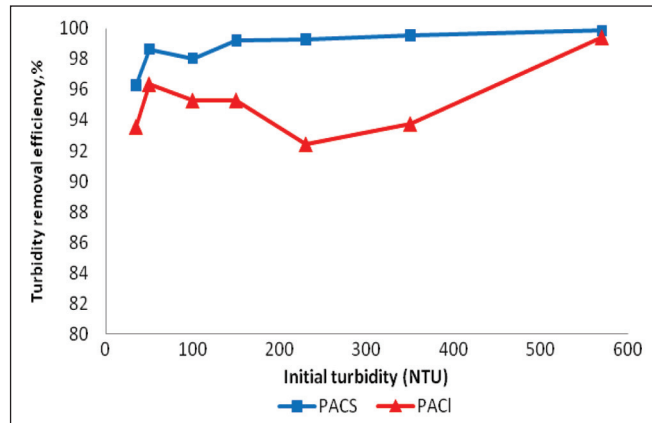


Figure 4: Effect of different turbidity levels on the turbidity removal by poly-aluminum chloride-sulfate and poly-aluminum chloride at pH 9.5, 6.5 and dosage 1.22, and 0.1 mmol/L as Al, respectively

reduce the turbidity removal efficiency.^[21] After that with increasing turbidity and in higher density colloidal particles, surface charge neutralization occurs and due to increasing the collision, the efficiency of turbidity removal increase.^[1,21,22] Metal-based coagulants, when added to water that has sufficient alkalinity, will hydrolyze into complex metal hydroxides in the form of $Me_q(OH)_p$ (Me =metallic ion). The counter ions form the coagulant, which can also be adsorbed onto the surface of the colloidal particles. Thus, the repulsive charges on the surface of the particles may be fully neutralized by charges carried out by the counter ions. Therefore, destabilized colloidal particles can adhere to each other to form colloidal-colloidal complexes.^[1] With additional turbidity increasing at a fixed coagulant dosage, adsorption sites on the solid metal hydroxide formed have low capacity, by colloidal particles saturate and turbidity removal efficiency is decreased again.^[1,10,11]

In the final stage due to the high presence of colloidal particles in the suspension, charge neutralization was not the only mechanism by which turbidity removal occurred, other mechanisms such as adsorption and particles bridging or sweep coagulation happened and turbidity removal efficiency is increased. In the case of PACS, the higher removals might be due to the sweep coagulation mechanism, which is inclined to occur at high PACS dosages.^[19]

CONCLUSIONS

The results of this study demonstrated clearly that PACS shows a superior coagulation-flocculation performance compared to PACl in most cases during turbidity removal, regarding to flocs size and removal efficiency, especially in high turbidity water. Optimum removal efficiency of turbidity occurred at a dosage of 0.1, and 1.22 mmol/L as Al, and optimum pH of 6.5 and 9.5 for PACl and PACS, respectively. At the optimum conditions for pH and dosages of both PACl and PACS, the turbidity removal efficiency could reach about 95.85% and 97.86%, respectively. For PACl and PACS, residual turbidity was highly dependent on the settling time. Most particles are removed in the first 5 min. The turbidity removal efficiency for the PACS was slightly higher than those for PACl at the same time. Different turbidity levels have a great effect on turbidity removal efficiency by both coagulants. Practically, due to the PACS usage in turbidity removal was about 10 times PACl, when using this coagulant type in the removal of turbidity from water the economical assessment should be necessary.

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