Flocculation of Turbid Water Using Polyferric-Based Composite Coagulant

K. H. Tan and S. H. Lai

Department of Civil Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.

E-mail: laish@um.edu.my

Abstract. The flocculation of turbid water using polyferric chloride-polydimethyldiallylammonium chloride (PFC-PDMDAAC) has been studied. Effect of preparation parameters basicity ratio (B ratio) of PFC and PDMDAAC/PFC ratio and operating parameters pH and dosage were investigated. PFC-PDMDAAC displayed maximum turbidity removal of 94.8% at 4.0mg/L when B=0.5 and PDMDAAC/PFC ratio= 7%. The best turbidity removal efficiencies by PFC-PDMDAAC were 84.7% at pH 7.5. These results reveal that PFC-PDMDAAC is efficient for flocculation of turbid water.

1. Introduction
Over recent decades, Malaysia faces many challenges in controlling the quality and quantity of stormwater runoff [1]. One way of controlling increased runoff due to urbanization and social-economic development is to build stormwater management facilities, such as retention/detention ponds. It is found that many of the ponds in Malaysia which are high in turbidity are suffered from a number of water pollution problems such as siltation and sedimentation and causes a number of social, health and environmental problems, such as disease, odor smell, poor aesthetic value in the surrounding area. Ponds can often dampen the impact of increased turbidity events by acting as points in a stream or river where particles can settle before being drawn into the intake of a treatment plant. Hence removal of turbidity is one of the major challenges in retrieving ‘dead pond’ in Malaysia.

Coagulation-flocculation is an important process in water treatment. Coagulation-flocculation is one of the conventional physico-chemical methods used to destabilize disperse particles in water [2]. Coagulants are added to aggregate destabilized colloidal particles into larger-sized flocs that can be effectively removed in subsequent separation processes [3]. Coagulants may be classified into inorganic and organic coagulants. With superior coagulation efficiency and high resistance to breakage in comparison to traditional metal salts, inorganic polymeric coagulants are most commonly used in water treatment. Conventional aluminum and ferric-based salts, such as polyaluminum chloride (PAC) and polyferric chloride (PFC), are widely used nowadays. Nonetheless high dosages are required and large volume of sludge is usually produced and high cost incurred [4]. Some researchers have focused on the use of organic polymer in water treatment, such as polydiallyldimethylammonium (PDADMAC). PDADMAC has shown superior coagulation performance in their wider optimum pH range and the lower dosage required for water treatment [5]. Organic polymeric flocculants have been used in water treatment for decades as coagulant aids after the addition of inorganic coagulants.

Conventionally, inorganic polymer and organic polymer are added to wastewater separately, requiring two reagent addition systems [6]. In order to utilize the advantages of both inorganic and organic coagulants to prepare more cheap, effective and environmentally friendly flocculants, research is recently focused on the development of composite inorganic-organic coagulants. Numerous
researchers were using composite flocculant, produced by combining inorganic coagulant with organic coagulant. [7-13].

In this study, turbidity removal efficiency of composite flocculant PFC-PD which is composed of polyferric chloride (PFC) and PDADMAC was measured in treating synthetic turbid water under different initial turbidity and pH. Besides the effects of basicity ratio (B, OH/Fe ratio) of PFC and weight percentage (w(P)) of PDADMAC was also investigated.

2. Materials and methods

2.1. Materials
Iron (III) Chloride, Polydiallyldimethylammonium chloride, sodium carbonate and disodium phosphate were obtained directly from Sigma-Aldich (Malaysia) Sdn. Bhd.

2.2. Preparation of coagulant
Firstly, a pre-determined amount of FeCl$_3$·6H$_2$O was dissolved in deionized water. After that, Na$_2$CO$_3$ powder was added to the ferric chloride solution to achieve desired basicity (B, OH/(Fe) ratio). Then, stabiliser Na$_2$HPO$_4$ (AR) was added to the solution. Finally, a measured amount of polydimethyl diallylammonium chloride (PDMDAAC) was injected to the above solution under strong stirring until all foam disappeared to prepare the composite coagulant PFC-PD. Three percentages (3.5%, 7.0% and 14%) of PDMDAAC by weight (Wp) in the flocculants were prepared.

2.3. Preparation of turbid water sample
Kaolin clay purchased from Kaolin (Malaysia) Sdn. Bhd. used to prepare turbid water samples. 1.5 g of kaolin was prepared in 5 L of distilled water by mixing for 24 hours to prepare the stock kaolin suspension. The turbidity of this sample was determined to be around 220-240 NTU. Lower turbidity samples were prepared by diluting this stock turbidity suspension of 150, 100 and 50 NTU turbidity values.

2.4. Coagulation Experiment
The jar test experiments were carried out using VELP Scientific JLT6 Leaching Jar Test with 6 1L beakers. 0.5L of turbid water sample was added into beakers and predetermined dose coagulant solution was introduced. The suspension solutions were mixed rapidly at 120 rpm for 3 minute and stirred slowly at 40 rpm for 15 minutes. The samples allowed to settle for 30 minute. The supernatant samples were taken and measured for final turbidity.

3. Results and discussions

3.1. Turbidity Removal Evaluation of PFC-PDADMAC under different initial turbidity
Clay suspension was prepared at 50NTU, 100NTU and 150 NTU turbidity values to represent low, medium and high turbidity and a series of experiments were conducted on them. To get better understanding of the potential usability of ferric chloride as coagulant and to determine the effect of the ferric chloride on different turbidity, ferric chloride concentration from 0.5mg/L to 3.0mg/L were dosed.

Figure 1 summarizes turbidity removal efficiency increased as the dose of PFC-PD increases until optimum turbidity removal was achieved. For low initial turbidity of 50NTU, when the PFC-PD dosage less than 2.0mg/L, the initial turbidity decreased sharply but beyond this optimum value, the final turbidity seems increased. The most effective removal of turbidity could be obtained there is just sufficient coagulant absorption on the fine particles. The presence of overdose would make the floc less settle able. Therefore turbidity removal efficiency decreased to 84.21% when the PFC-PD dosage increased to 3.0mg/L.
Figure 1. Turbidity removal efficiency for different initial turbidity using PFC-PD.

Even all three initial turbidity had the same optimum PFC-PD dosage range of 1.5mg/L to 2.0mg/L, it is investigated that the optimum range are boarder with the increasing of initial turbidity. There was a significant increasing of 23.9% in removal efficiency when the PFC-PD dosage increased to 2.0mg/L for 150NTU initial turbidity whereas there were only 16.17% and 12.97% removal efficiency for 100NTU and 50NTU. 50NTU initial turbidity had a narrower optimum range but showed a better effect on turbidity removal, that was 94.33% removal efficiency which is 2.6% and 9.0% higher than 100NTU and 150NTU initial turbidity.

3.2. Effect of basicity of PFC
In order to identify the optimum removal efficiency for PFC-PDADMAC, different [OH−]/[Fe], B value of polyferric chloride were prepared and investigated under constant pH 7 and initial turbidity of 100NTU as shown in Figure 2.
It is noted that the turbidity removal of PFC–PD was slightly influenced by basicity of PFC-PD. The maximal turbidity removal (94.8 %) was achieved by FeCl₃–PDMDAAC at a dosage of 4.0 mg/L. Figure 2 showed that the coagulation and charge neutralization ability decreased with basicity ratio is increasing until it reached optimum turbidity removal efficiency at dosage 4.0mg/L. Most of the Fe(III) hydrolysate shows in monomer and lower polymerization at lower basicity value. Fe(III) hydrolysate which is positively charged would be easier to be adsorbed on negatively charged particles by charge neutralization. When the $B$ value increases, the PFC hydrolysate transformed to hydroxide which has less positive charge and hence the turbidity decreased due to weak charge neutralization.

PFC-PD with higher $B$ value achieved gradual decrease in coagulation efficiency when PFC-PD was overdosed. Organic polymer PDMDAAC is a dominant positive charge in PFC-PD and the charge neutralization ability of PFC drops when $B$ value increases. Difference in charge neutralization ability between PFC and PDMDAAC extended and the proportion of particle surface sites which reacted with PDMDAAC increase. Therefore charge reversal was obtained by PFC-PD with higher $B$ value.

### 3.3. Effect of $w(P)$ of PDMDAAC

Figure 3 illustrates the turbidity removal efficiency of PFC ($w(P) = 0$) and PFC–PD ($B = 0.5$) with three different $w(P)$ (3.5%, 7.0%, 14.0%). It showed that turbidity removal increased dramatically with the increase of $w(P)$. This is because the higher weight percentage of PDMDAAC in PFC-PD could neutralize more negative charge on the particle surface and gave stronger charge neutralization compared to lower PDADMAC content. Besides, the PFC–PD with higher $w(P)$ showed stronger turbidity removal in a much narrower dosage range, which increased the difficulty in determining the optimum dosage in water treatment. Thus the PFC–PD with $w(P) = 14\%$ and above is not applicable.
3.4. Effect of pH on Turbidity Removal Efficiency

Turbid water sample of 150NTU initial turbidity was examined at various pH conditions (5.0, 6.0, 7.0, 7.5, 8.0 and 9.0). FeCl\textsubscript{3}, PDMDAAC with high \( M_w \), PFC with \( B=0.5 \) were selected for testing turbidity removal efficiency. The constant dosage used for all coagulants are 2.0 mg/L.

![Figure 3](image3.png)

**Figure 3.** Turbidity removal efficiency of PFC-PDADAAC for different PDADMAC weight content.

The highest turbidity removal efficiencies of PFC were 84.7\% at pH 7 and it showed that pH would affect the turbidity removal significantly. This instance was in good agreement with the previous finding. The floc patterns of Fe (III) coagulants were different under different pH conditions. The ability of Fe (III) coagulants to neutralize the negative charge and to sweep the contamination is optimal in the middle pH range.

![Figure 4](image4.png)

**Figure 4.** Turbidity removal efficiency of PFC-PDMDAAC for different PDADMAC weight content.
For PDADMAC, the turbidity removal efficiencies were mostly invariable in all pH range. All of the turbidity removal efficiencies were between 58.2% and 66.0% within the pH range of 5.0–9.0. The above phenomenon was in good agreement with previous study that PDMDAAC was not sensitive to pH within a fairly wide range of application.

It also could be observed that there were small changes in the turbidity removal rate of composite coagulant in all pH range. And the best turbidity removal efficiencies for treating high turbid water by PFC-PDMDAAC were 84.7% at pH 7.5. The results above indicate that using PFC–PDADMAC composite coagulant for treating high original pH would be more advantageous than using PFC coagulant.

3.5. Comparison of coagulation efficiency of PFC-PD with PFC, PDMDAAC and FeCl3

The coagulation efficiency of PFC-PD was compared with PFC, PDMDAAC and FeCl3 were compared in terms of turbidity removal efficiency as shown in Figure 5. Constant initial turbidity 150NTU was used throughout this session. The turbidity removal of FeCl3 and PFC increased gradually when the coagulant dosages increased. The coagulation efficiency of FeCl3 and PFC was much lower than PFC-PD composite coagulant for lower coagulant dosage. Only about 60% of turbidity removal could be achieved when the dosage increased to 3.0 mg/L. on the other hand, PDMDAAC showed better turbidity removal efficiency compared to FeCl3 and PFC within the dosage range 0.5–1.5 mg/L.

![Figure 5. Turbidity removal efficiency of various coagulants under 150NTU initial turbidity](image)

4 Conclusions

The composite coagulant PFC-PD was more efficient compared to FeCl3, PFC and PDADMAC in term of turbidity removal efficiency. Therefore, PFC-PD was more suitable for surface water treatment than conventional metal coagulants and organic polymers. Besides, the composite coagulant PFC-PD performed better coagulation performance at lower B value and higher w(P).

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