Citrus aurantiifolia and citrus microcarpa fruit peels waste as eco-friendly natural coagulants

Z Dollah¹, N A Sahat¹, N Hamzah¹, A A Musir¹ and R Ramli¹

¹Faculty of Civil Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500, Permatang Pauh, Pulau Pinang, Malaysia

Email: zuraisah@uitm.edu.my

Abstract. Turbidity is one of the importance of physical water quality parameter in the water treatment process. Aluminum sulfate (alum) and ferric chloride are the most widely groups of chemical coagulant and have been extensively used to remove turbidity. However, there are several flaws relates to the environmental issue and impose health risk to the consumer. Fruit peel waste as a natural coagulant is one of the alternative techniques in minimizing the usage of chemical coagulant in water treatment. This research focused on a combination of ratio 60:40 and 80:20 of citrus microcarpa peels and citrus aurantiifolia peels to act as a natural coagulant for turbidity removal. Furthermore, the effect of mixing duration is determined to establish the optimum mixing duration for the highest turbidity removal. Standard practice using jar test were performed in synthetic turbid water using kaolin. The highest turbidity removal occurred at optimum ratio of 80:20 with 77.6% efficiency removal where the optimum mixing duration was found to be at 120 rpm of rapid mixing at 3 minutes, 50 rpm of slow mixing at 20 minutes and 60 minutes of settling time. The study demonstrated that combination of citrus aurantiifolia peels and citrus microcarpa peels have the potential to be used as natural coagulant for a future alternative in water treatment.

1. Introduction

Turbidity is one of physical water quality parameter that needs to be treated before being distributed to consumer. Degree of clearness of water will classify the turbidity of the water. Usually turbidity consists of small particles that suspended in water such as clay, silts, tiny fragments of organic matter and microscopic organisms.

Coagulation is one of the vital processes in water treatment plant [1]. This process is achieved by addition of coagulants either chemical or natural which are used to aggregate particles into larger ones so that they settle easily to mitigate their removal [2]. Aluminum sulphate (alum) and ferric chloride are the most widely used groups of chemical coagulant and have been extensively used to remove turbidity. Furthermore, these two chemical coagulants are globally used in water and wastewater treatment. Despite its efficacy there are several major drawbacks when using aluminum sulphate. Aluminum produces large volume of sludge and reacts with natural alkalinity present in water leading to pH reduction. In 2001, Divakaran [3] reported the sludge acquired from utilizing aluminum salts prompt to disposal problems for example, aluminum aggregation in nature. Besides that, the investigations have announced that leftover alum may initiate Alzheimer's illness. In an investigation into alum, [4] also reported the same drawbacks. Mallevialle [5] Discusses the synthetic organic polymers, such as acryl amide, have neurotoxin and carcinogenic effects. In her case study of alum,
Anastasakis [6] identifies slime form in water treatment plants amid flocculation-coagulation with synthetic polymers has a constrained potential for reusing in light of the non-biodegradability of synthetic polymers.

Other researchers, Asrafuzzaman [7] however, have identified natural coagulant as safe, eco-friendly and generally toxic free. Thus, can reduce amount of sludge produced [8]. Treatment in sludge and handling costs can be much lower and approach to more sustainable option. It is environmental-friendly especially for the aquatic live compared to chemical coagulants. The raw plant-based coagulant can be obtained locally and hence, there are not consume much cost to obtain and maintain as they are renewable resource. [9] also claimed that natural coagulants are also non-corrosive. Till now, moringa oleifera, strychnospotatorum and phaseolus [10] are the most common plant-based natural ingredients studied by researchers worldwide. Previous studies also have proven the ability of plants such as cactus latifaria [11] and roselle seed [12] as the agent of turbidity removal.

Citrus species is the most popular worldwide fruits and is from the Rutaceae family [13]. In Malaysia, citrus microcarpa is known as calamansi lime and citrus aurantiifolia, is known as a key lime. It is believed to have originated in northern India and adjoining parts of Myanmar, or in northern Malaysia. This type of fruit is widely used in Malaysia, mainly serve as juice, foods flavor, medicinal application and the peels are mostly thrown away [14]. The benefits of citrus fruit have mainly been attributed to the presence of bioactive compounds, such as phenolics (flavonone glycosides, hydroxycinnamic acids), ascorbic, citric acids, and carotenoids [14 -15]. Most of the recent studies are focusing on the individual performance of citrus aurantiifolia and citrus microcarpa as fruit waste coagulant. However, very few studies attempted in investigating the combination of these two fruit wastes. Although numerous researches have been carried out on the plant-based natural coagulants, the mechanism of different mixing durations has not been established.

This research focused on the optimum dosage of turbidity removal using combination of citrus microcarpa peels and citrus aurantiifolia peels at different ratio, the percentage of turbidity removal and optimum mixing duration. The combination ratio of citrus microcarpa peels and citrus aurantiifolia peels are 80:20 and 60:40 and optimum dosage are determined from each ratio.

2. Material and methods

2.1. Sample collection

The peels used for this research are citrus aurantiifolia peels and citrus microcarpa peels obtained from fruit waste generated from restaurants in front of Universiti Teknologi Mara (UiTM) Pulau Pinang. An airtight container was left at the kitchen of the restaurant and was collected daily.

2.2. Preparation of peels

Peel extract was prepared according to procedure used by Šćiban [16]. The pulps are removed, and peels are cleaned with tap water then followed with distilled water. The peels were dried in the oven to dry for six hours at 105° temperature to get the peels in crispy state. Dried peels are shown in figure 1. The peels are grinded by using conventional grinder as shown in Figure 2 until it become powder form. Then, the powder form peels are sieved using 0.425 mm sieve.
2.2.1. Preparation of stock solution
The first ratio which is ratio 80:20 consist of 40 g of *Citrus microcarpa* peels and 10 g of *citrus aurantiifolia* peels in powder form were weight and suspended in 1 mol/L of sodium chloride (NaCl) solution. The solution was stirred using magnetic stirrer, and then filtered through a filter paper and the retained filtrates represented crude extract. The crude extracts are in yellowish colour however, colour may increase the turbidity of synthetic water. Therefore, distillation process was done to neutralize the colour into clear solution. Distillation unit K-350/K-355 as shown in Figure 3 was used for distillation process where transition process from liquid-gases-liquid occurred. The process is repeated for another ratio that consists of 30 g of *Citrus microcarpa* peels and 20 g of *Citrus aurantiifolia* peels.

2.3. Preparation of synthetic water sample
Six beakers of synthetic water sample were prepared one at a time by adding 0.3 g of kaolin into each 500 ml of tap water. The synthetic water samples were stirred to allow complete mixing of kaolin and tap water and the initial turbidity reading are recorded.

2.4. Jar test
This test is widely available and has been used in many investigational studies. The jar test method is one of the practical ways due to its simplicity and performances on coagulation process. Each beaker was filled with 500 ml of kaolin suspension as shown in figure 4. The coagulants were added into the beakers with corresponding to a dosage of 0 (control), 0.5, 1.0, 1.5, 2.0 and 2.5 mg/L. The appropriate
amount of hydrochloric acid (H_2SO_4) or sodium hydroxide (NaOH) was added to the beakers that would yield a final pH of 6.5.

The samples were mixed at three different speed and duration and were let settled accordingly. The process is repeated with ratio 80:20 with same three set of mixing duration. The proposed mixing duration are decided based on previous study that achieved high efficiency turbidity removal [17] [12].

| Mixing duration | Mixing speed (rpm) & mixing duration (min) |
|-----------------|--------------------------------------------|
| 1               | 80 rpm - 1 min 30 rpm - 15 min Settle - 20 min |
| 2               | 100 rpm - 4 min 40 rpm - 25 min Settle - 30 min |
| 3               | 120 rpm - 3 min 50 rpm - 20 min Settle - 60 min |

**Figure 4. Jar test apparatus.**

### 2.5. Laboratory testing (turbidity removal)

The laboratory testing was conducted to find the initial turbidity and final turbidity of water tested. Turbidity was measured using turbidity meter (2100Q Portable Turbidimeter) and it was expressed in Nephelometric Turbidity Units (NTU). The efficiency of turbidity removal is calculated using equation (1).

\[
\text{Turbidity removal efficiency (\%)} = \frac{T_i - T_f}{T_i} \times 100
\]  

(1)

where;

- \(T_i\) = initial turbidity
- \(T_f\) = final turbidity
3. Result and discussion

Table 2 shows a comparative study of turbidity reduction efficiency of coagulants using Citrus microcarpa and Citrus aurantiifolia peels extracts corresponding to the different ratio of 60:40 and 80:20. Using ratio 60:40 of citrus microcarpa and citrus aurantiifolia peels.

Table 2. The turbidity removal efficiency at different ratio of citrus microcarpa and citrus aurantiifolia.

| Ratio Citrus Microcarpa: Citrus Aurantiifolia | Mixing Duration (MD) | Dosage mg/L | Initial turbidity (NTU) | Final turbidity (NTU) | Turbidity removal (%) |
|---------------------------------------------|----------------------|-------------|-------------------------|-----------------------|------------------------|
| 60:40                                       | 1                    | 0           | 49.80                   | 50.2                  |                        |
|                                             | 1                    | 0.5         | 55.10                   | 44.9                  |                        |
|                                             |                      | 1.0         | 45.50                   | 54.5                  |                        |
|                                             |                      | 1.5         | 45.80                   | 54.2                  |                        |
|                                             |                      | 2.0         | 45.30                   | 54.7                  |                        |
|                                             |                      | 2.5         | 44.30                   | 55.7                  |                        |
|                                             |                      | 0           | 51.8                    | 53.8                  |                        |
|                                             |                      | 0.5         | 40.6                    | 63.8                  |                        |
| 80:20                                       | 2                    | 1.0         | 40.1                    | 64.2                  |                        |
|                                             |                      | 1.5         | 40.0                    | 64.3                  |                        |
|                                             |                      | 2.0         | 46.5                    | 58.5                  |                        |
|                                             |                      | 2.5         | 45.0                    | 59.8                  |                        |
|                                             |                      | 0           | 26.4                    | 76.8                  |                        |
|                                             |                      | 0.5         | 33.3                    | 70.8                  |                        |
|                                             |                      | 1.0         | 32.1                    | 71.8                  |                        |
|                                             |                      | 1.5         | 32.7                    | 71.3                  |                        |
|                                             |                      | 2.0         | 28.2                    | 75.3                  |                        |
|                                             |                      | 2.5         | 26.0                    | 77.2                  |                        |
|                                             |                      | 0           | 38.2                    | 67.6                  |                        |
|                                             |                      | 0.5         | 40.9                    | 65.3                  |                        |
| 80:20                                       | 3                    | 1.0         | 35.3                    | 70.0                  |                        |
|                                             |                      | 1.5         | 40.8                    | 65.4                  |                        |
|                                             |                      | 2.0         | 34.1                    | 71.1                  |                        |
|                                             |                      | 2.5         | 34.6                    | 70.7                  |                        |
|                                             |                      | 0           | 39.3                    | 66.4                  |                        |
|                                             |                      | 0.5         | 41.7                    | 64.4                  |                        |

The highest turbidity removal is 77.2% with 2.5 mg/l of coagulant dosage. Based on ratio 80:20, the highest turbidity removal was found 77.6% with 0.5 mg/l dosage of coagulant. Results indicate that the peel extract demonstrated good performance in improving the quality of water in terms of turbidity removal. As can be seen in Table 2, ratio 80:20 has higher turbidity removal compared to
ratio 60:40. It shows that combination of *citrus aurantiifolia* peels and *citrus microcarpa* peels have high potential to reduce turbidity in water. A possible reason of ratio 80:20 have higher turbidity removal is amount of *citrus microcarpa* are higher than *citrus aurantiifolia*. Optimum turbidity removal for this ratio is 77.60% and slightly lower than study reported by Seghosime et al [18] which is 84%.

3.1. Effect of mixing duration on turbidity removal

Figure 5 and Figure 6 shows graph of dosage of coagulant against percentage turbidity removal (%) using different mixing duration for ratio 60:40 and 80:20 respectively. Using ratio 60:40 mixing duration 3 indicate highest turbidity removal 77.2 %, whereas using ratio 80:20 mixing duration 3 shows same pattern of highest turbidity removal with 77.6 %. Mixing duration 3 have longer duration where mixing process at 120 rpm for 3 minutes duration. Purpose of rapid mixing is to ensure complete dispersion of the coagulant to aid the formation of flocs. The mixing then reduces to slow mixing which is 50 rpm for 20 minutes to allow the flocculation process. Purpose of flocculation is to enhance the collision between flocculent and colloids particle. Decreasing in mixing speed is to increase the contact surface between coagulant particles to promote collisions. Then, the settling time is the longest which is 60 minutes. In settling duration, the flocs are let settled at bottom of beaker by gravity. The proposed mixing duration are decided based on previous study that achieved high efficiency turbidity removal. Mixing duration 1 result in percentage of turbidity removal 98.8%, mixing duration 2 resulting 99.4% turbidity [17]. Lastly mixing duration 3 resulting 99.1% [12]. In an investigation which set out to decide quick blending, Kan et al [19] found that the ideal opportunity for fast blending influences the destabilization for the colloid and the downstream conglomeration of particles. Sufficient time for fast blending is dictated by utilizing a photometric dispersion analyzer (PDA) test to observe the aggregation. Overall, comparing the three results of mixing duration, it indicates that ratio 80:20 and mixing duration 3 are the best parameter to remove turbidity with the highest percentage of turbidity removal which is 77.56%. It was hypothesized that participants with a history of roselle seed with same mixing duration 3 producing excellent efficiency on turbidity reduction. Longer settling duration also promotes higher turbidity removal. This is due to the settling behavior of the suspended particles where it agglomerates into a bulk and forming settled particles at the bottom [20].

![Figure 5](image_url) **Figure 5.** Turbidity removal for ratio 60:40 of natural coagulant.
4. Conclusion

Based on mixing duration intensity and ratio using natural coagulant and the highest turbidity removal among ratio 80:20, 60:40 from mixing duration 3 was determined. *Citrus microcarpa* and *citrus aurantiifolia* peels were found to have high potential to remove turbidity from 134 NTU to 30 NTU at optimum dosage of 0.5 mg/L. The highest percentage of turbidity removal was ratio 80:20 where 77.6% of turbidity removal. Optimum mixing duration were found at rapid mixing is 120 rpm at 3 min and slow mixing is 50 rpm at 20 min for the highest of turbidity removal The study has confirmed to the findings of Seghosime et al [18] which found that *citrus aurantiifolia* is suitable for water turbidity treatment.

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