Evaluation and optimization of the coagulation-flocculation process using conventional rice starch in potable water treatment

S-C Chua¹², F-K Chong³, C-HYen⁴, Y-C Ho¹²*,

¹Civil and Environmental Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia.
²Centre for Urban Resource Sustainability, Institute of Self-Sustainable Building, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia.
³Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia
⁴Department of Water Resource Technology & Materials Research, Division of Water Technology Research, Industrial Technology Research Institute, Taiwan.

* yeekchia.ho@utp.edu.my

Abstract. In this study, the application of conventional rice starch as coagulant in potable water treatment has been assessed. Rice starch was found to gelatinize at 83 °C for effective flocculation. Besides, respond surface method (RSM) was used to identify the significant factors and to optimize the turbidity reduction in potable water treatment. pH, dosage of starch and settling time were identified as significant factors. To achieve the maximum turbidity reduction (89%), the optimum conditions of the factors are with 9.64 mg/L dosage of starch, 20 min of settling time and pH 3. Interestingly, increase of dosage of starch can reduce up to 20 times of settling time which enhance the feasibility of starch to use in the potable water treatment industry. Validation test was conducted to validate the predicted data from designed model.

1. Introduction
Water treatment had been developed since 500 BC, where bag filter was first invented to trap sediments in the water. After that, coagulation process using aluminium sulphate (alum) has been discovered by Egyptians to remove the pollutant in the water. Due to its excellent efficiency in removing the pollutant, coagulant process using alum as coagulant is still widely used in most of the water treatment [1]. Despite of the efficiency of the process, the coagulant that used in the process poses two non-negligible disadvantages in human health and environmental aspect. In 1986, two studies that conducted parallelly in Norway have revealed the potential risk of the aluminium in the drinking water to cause Alzheimer Diseases (AD). Subsequently, several epidemiological studies have proven the relationship between the AD and the aluminium that retained in the drinking water [2, 3]. Apart from health issue, the use of chemical coagulant in coagulation process generated large amount of sludge which increase waste management cost and not environmentally friendly as well [4]. These disadvantages and limitations have motivated researcher to search for safer, eco-friendly and natural material. Recently, natural
coagulant that extracted from animals, plants or microorganisms have been focused as the replacement of the chemical coagulant as they are generally eco-friendlier and safer to human health. Various plant-based coagulants have been discovered e.g. *Moringa oleifera* coagulant, *Mangifera indica* coagulant [5], *Citrus sinensis* coagulant [6], Phoenix dactylifera coagulant etc. Starch has been proven to be an effective coagulant in several applications i.e. agro-industrial wastewater where 84.1 % TSS removal is achieved by solely dosage of starch [7]. Several researches carried by Choy, et al. [8] have investigated the potential of conventional rice starch in turbidity removal using synthetic water (close to 50 % of turbidity reduction). Although the result reveals the potential of rice starch in turbidity reduction, the actual efficiency of the rice starch in potable water treatment is still unknown. Therefore, this paper aims to investigate the performance of the rice starch in potable water treatment and optimize the operating conditions to evaluate the feasibility of rice starch to be applied in water treatment industry.

2. Material and method

2.1. Starch preparation
Rice starch was obtained from the grocery shop and used without further purification. The starch solution of 3 g/L was prepared by dissolving 1.5 g of starch into 500 mL of distilled water. The solution was agitated at 300 rpm and heated to specific temperature for gelatinization purpose. The starch was freshly prepared in each day to avoid biodegradation. The temperature for starch gelatinization was investigated and observed through microscope (LEICA DM LB2).

2.2. Sampling of river water
River water is sampled at the Sultan Idris Shah II Water Treatment Plant (4.483440, 100.913978) in Perak, Malaysia on 10 October 2018. Due to drizzling rain the day before, the average turbidity of the samples is slightly high, 200 Nephelometric Turbidity Unit (NTU). The samples are transported and store at 4 °C.

2.3. Assay of turbidity reduction
Convectional 6 jar apparatus (VELP Scientifica JLT6, Italy) were used for jar test experiment. 200 ± 5 NTU turbidity of river water was filled into beaker followed by pH adjustment using 1.0 M HCl or 1.0 M NaOH to obtain desired pH value. Desired amount of rice starch was added afterward. The water was mixed for 1 min with 150 rpm (fast mixing), followed by slow mixing with 30 rpm for 20 min. At the end of slow mixing, the beakers were transferred to flat environment and left undisturbed for desire amount of time. 10 mL of water was withdrawn after from each beaker and the turbidity of the water was measure in triplicates for comparison using HACH 2100 Q turbidity meter.

2.4. Screening and Optimization through Design of experiment (DOE)
Most of the researchers no longer afford to experiment in a traditional way for screening and optimization process, changing one factor at a time. The traditional method is not only time consuming, but the relationship of each factor is hard to be determined as well. Therefore, a far more effective method, design of experiment (DOE) was adopted for screening and optimization process. DOE is a systematic and computer-enhanced approach to analyse the interaction and the relationship between factors that affecting a process simultaneously [1]. In this research, screening experiment was carried out to determine the important factors. For optimization experiment, Box-Behnken design (BBD) was adopted to optimize three factors which are (1) pH, (2) dosage of starch, and (3) settling time. Each factor is set to two level, low limit and high limit for analysis purpose. The low limit and high limit of each factor for screening and optimization process are illustrated in table 1.
Table 1. Low limit and high limit for factorial design.

| Factors       | Low limit | High limit |
|---------------|-----------|------------|
| pH            | 3         | 9          |
| Dosage of starch | 0.1      | 40         |
| Settling time | 1         | 20         |

3. Results and discussion

3.1 Rice starch gelatinization

According to the study carried out by Choy, et al. [8], starch gelatinization process is important to ensure effective coagulation-flocculation process. However, the gelatinization temperature (GT) is varied according to the type of starch, specifically, the amylose and amylopectin ratio of the starch. The GT of conventional rice starch used in this research was investigated through microscope. The rice starch particles do not dissolve in the water at room temperature, 25°C and can be clearly observed as shown in figure 1(a). However, when the starch solution is heated, the amorphous space of the starch particle absorbed the water causing the starch particle to swell. At 83°C, the water no longer allows to enter to the crystalline regions. The heat caused the region to become diffuse, which allow amylose chains to separate into an amorphous form and the number of the crystalline regions gradually decreases [9]. When the amylose molecules leach into the water, the granule structure of the starch disintegrated which caused the starch loses its birefringence and its extinction cross under microscope as illustrated in figure 1(b). The amylose and amylopectin that separated from the starch helps in the bridging during flocculation process [8].

![Figure 1](image)

Figure 1. Rice starch (a) 25°C, (b) 83°C under microscope observation (20X magnification).

3.2 Screening (factorial design)

12 experiment runs with four centre points have been generated from the Design Expert software and the ANOVA result is illustrated in table 2. In statistically approach, p-value is used to determine the factor that will significantly affect the process. The factor with p-value less than 0.05 is considered significant. The p-value of dosage of starch, pH and settling time factors are 0.0049, 0.0001 and 0.0013 respectively, which indicate all three factors are significantly affect the process. Besides, the 0.0001 p-value of model indicated high reliability of the model. The high reliability of model was further proven by the model 0.999 R-squared value, which close to 1. The R-squared obtained indicate that 99.9% of the variation is well-explained and only 0.001 of variations were not explained by the model.
### Table 2. ANOVA table for screening process (factorial design).

| Sources                      | Sum of Squares | Mean Square | F Value   | p-value | Remarks   |
|------------------------------|----------------|-------------|-----------|---------|-----------|
| Model                        | 4334.28        | 619.18      | 568.36    | < 0.0001| Significant|
| Dosage of Starch             | 34.53          | 34.53       | 31.69     | 0.0049  | Significant |
| pH                           | 4209.42        | 4209.42     | 3863.92   | < 0.0001| Significant |
| Settling Time                | 70.55          | 70.55       | 64.76     | 0.0013  | Significant |
| Dosage of Starch × pH        | 1.64           | 1.64        | 1.50      | 0.2874  | -          |
| Dosage of Starch × Settling Time | 8.73           | 8.73        | 8.01      | 0.0473  | Significant |
| pH × Settling Time           | 9.20           | 9.20        | 8.44      | 0.0439  | Significant |
| Dosage of Starch × pH × Settling Time | 0.23       | 0.23        | 0.21      | 0.6701  | -          |

* R-Squared: 0.999

### 3.3 Optimization of operation conditions

The three significant factors are optimized through Box-Behnken design (BBD) and the ANOVA result is shown at table 3. The results obtain is similar with screening result where the model and the three operating factors are significant with the p-value less than 0.05. The model is reliable due to few reasons (i) R-squared of the model is 0.98 which indicate that 98 % of variance is perfectly explained, (ii) Lack of fit of the model is not significant (p-value: 0.1190) which reveals that the model is adequate to predict the turbidity reduction within the designed range, and (iii) Data are normally distributed as shown in figure 2 which indicate the normal distribution appears to be a good model for the data [10, 11]. In term of the interaction between the factors, dosage of starch shows a significant interaction with settling time (p-value 0.0477).

### Table 3. ANOVA table for optimization process.

| Sources                      | Sum of Squares | Mean Square | F Value   | p-value | Remarks   |
|------------------------------|----------------|-------------|-----------|---------|-----------|
| Model                        | 3129.37        | 347.71      | 34.17     | 0.0006  | Significant |
| Dosage of Starch             | 123            | 123.00      | 12.09     | 0.0177  | Significant |
| pH                           | 2139.85        | 2139.85     | 210.30    | < 0.0001| Significant |
| Settling Time                | 302.66         | 302.66      | 29.74     | 0.0028  | Significant |
| Dosage of Starch × pH        | 2.81           | 2.81        | 0.28      | 0.6219  | -          |
| Dosage of Starch × Settling Time | 69.30         | 69.30       | 6.81      | 0.0477  | Significant |
| pH × Settling Time           | 35.74          | 35.74       | 3.51      | 0.1198  | -          |
| Dosage of Starch × Dosage of Starch | 9.89         | 9.89        | 0.97      | 0.3695  | -          |
| pH × pH                      | 431.49         | 431.49      | 42.41     | 0.0013  | Significant |
| Settling Time × Settling Time| 0.014          | 0.014       | 1.351E-003| 0.9721  | -          |
| Residual                     | 50.88          | 10.18       |           |         | -          |
| Lack of fit                  | 46.75          | 15.58       | 7.56      | 0.1190  | -          |
| Pure Error                   | 4.12           | 2.06        |           |         | -          |

* R-squared: 0.98
RSM is useful to optimize the operating conditions especially for industrial purpose in order to reduce the operating cost in the meanwhile maintaining the quality. The optimum conditions (within the designed range) of > 89% of turbidity reduction are with 9.64 mg/L dosage of starch and 20 min of settling time at pH 3 as shown in the figure 3. Besides, increasing the dosage of starch can greatly reduce the settling time, meanwhile, achieved the similar result. As shown in figure 4, 89% turbidity reduction can be achieved as well with 40 mg/L dosage of starch and 1 min of settling time at pH 3. The settling time is reduced to 20 times lower which greatly enhance the feasibility of starch to use in the water treatment industry. However, pH 3 may not economical feasible in most of the water treatment plant. Therefore, another set of optimum conditions is generated, and the range of the pH is strictly set to pH 6.5 – pH 9 as shown in figure 5. The maximum turbidity reduction can be achieved within the specific range is 63.62% and the optimum condition are with pH 6.5, 19.41 mg/L of starch, and 20 min of settling time.

**Figure 2.** Normal plot of residuals (based on different experiment runs)

**Figure 3.** The optimum conditions generated by the Design Expert software (within designed range).
3.4 Validation
To validate the reliability and accuracy of the model, the predicted result of the three random runs chosen from the software are compared with the actual result obtained from the experiment. As shown in Table 4, all the differences between predicted and actual turbidity reduction are less than 2 %. The low percentage of differences reveal the high accuracy of the model and the predicted results by the software.

Table 4. Validation experimental runs.

| Runs | Dosage of starch (mg/L) | pH  | Setting time | Turbidity reduction (%) | Differences (%) |
|------|-------------------------|-----|--------------|-------------------------|-----------------|
| 1    | 9.64                    | 3   | 20           | 89.83                   | 88.72           | 1.11            |
| 2    | 5.94                    | 7.3 | 5            | 44.48                   | 46.28           | 1.80            |
| 3    | 36.57                   | 4.6 | 4            | 70.33                   | 71.08           | 0.75            |

4. Conclusion
From the present set of experiments, conventional rice starch after gelatinization has potential as a source of green and eco-friendly natural coagulant for potable water treatment. The maximum turbidity
reduction was found to be 89 % with the optimum conditions of 9.64 mg/L dosage of starch and 20 min of settling time at pH 3. It was concluded that the use of conventional starch as coagulant for turbidity removal might be preferred because of their non-toxic nature, abundance and low capital cost as compared to others coagulant.

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