Performance Study of Watermelon Rind as Coagulants for the Wastewater Treatment

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Abstract. The scarcity of fresh and hygienic water sources leads to a demand of more research for the treatment of wastewater. One of the possible ways is using a watermelon rind as a natural coagulant where its performance was investigated in terms of turbidity, pH and BOD. Watermelon rind (WR) and alum(A) at different compositions (WR100, WR50A50, WR70A30, A100) were introduced in the synthetic wastewater before treated on natural wastewater by jar test. Results revealed that the turbidity, pH as well as dissolved oxygen level were highly dependent on the coagulant dosage. About 90% of turbidity was reducing at 70% of powdered watermelon rind and 30% alum (WR70A30) on the contrary only 72% in natural wastewater. In addition, WR70A30 had better reduction in turbidity as compared to using 100A. On the other hand, final pH reading falls approximately in the range of 6 to 8, respectively which is acceptable for the standard wastewater discharge. Meanwhile, the results for the BODs for the natural wastewater is in the ranges between 0.35 to 1.39 had met the WHO standard. Finally, the FTIR analysis on treated and untreated watermelon rind confirms similar peaks of functional groups. Overall, the present study on WR as coagulant show a good performance in treating both natural and synthetic wastewater.

1. Introduction

In Asia and Pacific region, it was estimated that an amount of 80% to 90% of wastewater is left untreated and thus, polluting land and affecting the ecosystems [1]. Therefore, wastewater treatment is one of the best solutions to ensure that the wastewater can return to the water cycle with less impact to the environment and society [2]. Generally, the conventional water treatment system includes but not limited to; aeration, solid separation, coagulation, flocculation, filtration and disinfection. However, in the present study, the coagulation was used to remove the small particle and colloidal which causes high turbid water which is undesirable in wastewater [3 ; 4].

Conventional chemical coagulants such as aluminium sulphate (alum), aluminium chloride, ferric sulphate, ferrous sulphate and sodium aluminate were widely used as coagulants. However, it creates additional environment and health problems. For example, Aluminium-based coagulants have led to dementia and Alzheimer [4]. Besides, treating wastewater using aluminium is somehow no longer practical as it produces large amount of sludge from high concentration of remaining aluminium in treated water [5]. Meanwhile, sulphate-based coagulants may stain the water treatment equipment, giving out a brownish colour on the equipment. On the other hand, a chloride-based coagulant is highly corrosive and generates quite large amount of sludge upon treatment of wastewater.
Thus, several studies had been introduced using natural coagulants such as white propinac, watermelon seed, cassava and moringa seeds which is very effective [4][6][7]. Moreover it is locally available, safer, and more environment friendly than artificial coagulants [8]. Besides, the sludge produced is lower 20% to 30% than alum, highly biodegradable and free from toxin. In the present study, watermelon (Citrullus lanatus) was introduced as natural coagulants due to several reasons. Watermelons can be easily obtained in almost all supermarkets and fruit stalls especially during hot and dry weather in Malaysia. As it is a favourite fruit to consume daily, it produces waste at the supermarkets and household garbage. Besides, watermelon rind was found as a good adsorbent in removal of heavy metals ions in wastewater [5][9][11]. However, in the removal of turbidity, the seed was used as a coagulant instead of the rind [7][12][13].

In the coagulation process, suitable conditions should be set to obtain optimum removal such as the dosage and pH. The optimum turbidity removal for watermelon seed was found about 0.1g/L and in another study, about 20% alum is needed to achieved the best turbidity [6]. The high removal also can be obtained when the dosage for natural coagulant exceeding the amount of artificial coagulant [5][7][14]. The used of watermelon rind in the present study is due to the good performance of fruit rind in binding metal ions. It might be contributed by its ability to bind the metal ions forming complexes by giving an electron pair [16]. To achieved higher removal, the natural coagulant can be treated with acid or bases such as nitric acid and sodium chloride to obtain pH 7 [4]. In addition, coagulants extraction, solubility, coagulants, charge on particles and basicity of a coagulant also can be affecting on coagulation process. Meanwhile, there also other factor should be considered such as settling time, turbulence, rapid and slow mixing. In the present study, the potential and effectiveness of watermelon rind as a natural coagulant for wastewater treatment was carried out to evaluate its effectiveness in the reducing turbidity, pH, temperature and oxygen level changes for the treated water. Finally, the coagulation process was compared between synthetic and natural waste water.

2. Material and method

2.1. Material

The waste watermelon (Citrullus lanatus) rind as a coagulant were obtained from the local market in Pasir Gudang. The Aluminium Sulfate (Emory) or known as alum, a well-known chemical-based coagulant for the wastewater treatment. Analytical grade acid nitric (HNO₃) was used and working solution were prepared using Milli-Q water (Millipore SAS, 67120 Molsheim, France).

2.2. Preparation coagulants

The watermelon rind was washed thoroughly using tap water and Milli-Q water to remove impurities before cutting it into small pieces. It was then sun dried before heated in an oven at 60°C for 24 hours. The dried watermelon was ground and sieved to obtain constant size of 500 µm and was stored at room temperature before use. Coagulant solutions were prepared at varying dosage composition of watermelon rind (WR) and alum (A) as in Table 1. The powdered WR was added into 0.3M HNO₃ to obtain pH 7 and was allowed to settle for 24 hours. The mixtures were then washed with Milli-Q water and filtered. The filtrate was then used according to the dosage stated in Table 1, where the percentage of coagulants shown is in terms of mass.

2.3. Wastewater Preparation

The effectiveness of the coagulants in the present study was introduced to two different types of wastewater, natural wastewater and synthetic wastewater. The natural wastewater was collected from the lake at UiTM Pasir Gudang. The collected wastewater was kept refrigerated at 6°C before use to avoid degradation of the water. The initial turbidity and pH of the collected water were measured. The synthetic wastewater was prepared by dissolving 0.5 g of powdered Bentonite clay in 1000 mL Milli-Q water to make 0.5% Alum stock solution (Aluminum Sulfate Hydrate express in mg/L).
Table 1. Field layout for coagulant doses.

| Sample number | Dosage Mixtures   | Percentage of Dosage          |
|---------------|------------------|------------------------------|
| 1             | Control          | No coagulant                 |
| 2             | WR100            | 100% Watermelon Rind         |
| 3             | WR50A50          | 50% Watermelon Rind, 50% Alum|
| 4             | WR70A30          | 70% Watermelon Rind, 30% Alum|
| 5             | WR30A70          | 30% Watermelon Rind, 70% Alum|
| 6             | A100             | 100% Alum                    |

2.4. Jar Test
The batch test was carried out using a conventional jar test apparatus (Velp Scientifica JLT6) with six different beakers in 1000 mL of wastewater at varying coagulants dosage. Firstly, the sample was mixed homogenously and then, the sample was stirred vigorously as follows: 2 minutes rapid mixing at 250 rpm for coagulation and 15 minutes slow stirring at 50 rpm for flocculation before the content was left to settle for one hour [4]. The 100 mL supernatant was collected using a syringe from 3 cm below the water surface for sample analysis.

2.5. Analytical measurement
The turbidity reading was taken before and after the jar test using turbidimeter (Lovibond). The sample was thoroughly shaken for 30 seconds to eliminate air bubble. The samples were then put in the sample chamber to measure the turbidity. The turbidity reduction percentage was calculated using equation (2).

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\text{Turbidity} = \frac{\text{Initial turbidity} - \text{Final turbidity}}{\text{Initial turbidity}} \times 100\% \quad (1)
\]

The initial pH level for the treated water was taken before the wastewater was treated with the coagulants using a pH meter (Eutech Instruments). Meanwhile, the final pH value for the wastewater was recorded two hours after treatment. The dried WR treated with HNO₃ and WR untreated were analysed at 400-5000 cm⁻¹ using Bruker Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy to determine its functionality changes.

3. Results and discussion
Table 2 shows the initial parameter results for the freshwater taken from the lake at UiTM Pasir Gudang. Results show that the initial sample of freshwater and synthetic water represent a higher value than the standard WHO for drinking water.

3.1. Turbidity
Turbidity is a measure of degree to which the water loses its transparency due to the presence of suspended particulates. The acceptable WHO for turbidity is maximum 5 NTU. The percentage of turbidity reduction was shown in Figure 1.
Table 2. WHO drinking water standards.

| Parameter         | Initial freshwater | Initial synthetic water | WHO standards |
|-------------------|--------------------|-------------------------|---------------|
| Turbidity (NTU)   | 33.2               | 123                     | 5 Max         |
| Temperature (℃)   | 30.4               | 28                      | 25 - 30       |
| pH                | 9.35               | 6.83                    | 6.5 - 8.0     |
| BOD (mg/L)        | 7.5                | 1.33                    | 3 - 5         |

Figure 1. Percentage reduction of turbidity in synthetic and natural wastewater.

Results for the turbidity of synthetic and natural wastewater were compared to the WHO standard in Table 1. It shows that the percentage of turbidity reduction is higher which can be achieved almost 90% reduction using watermelon rind. Since experiments were conducted on the variation of dosage only, it is expected that the results would be better and can meet the maximum 5 NTU for drinking water if other conditions were considered. This is because the settling time, turbulence and particle types are other factors that may affect the properties of the final wastewater [17]. Among all the dosage, the higher reduction was found on the WR70A30 and the lowest reduction is when WR100 was used. The percentage reduction of turbidity was only 48% for WR100. The descending highest turbidity reduction is as follows; 88% for WR50A50, 85% for WR30A70 and A100 and 50% for control sample. Results also show the similar reduction trend (WR70A30>WR50A50>A100>WR30A70>WR100) when the coagulant was introduced on the both natural and synthetic wastewater. However, the reduction in the natural wastewater is lower than the synthetic wastewater. At WR70A30 the percentage reduction on turbidity in natural wastewater is only 72% as compared to 90% in the synthetic wastewater and is slightly higher than A100 in synthetic wastewater.

Based on the results for turbidity, it can be concluded that the best dosage coagulant mixtures were at WR70A30. Moreover, to make it sustainable, the dosage mixtures of watermelon rind coagulant should exceed artificial coagulant or should be at the same dosage to obtain optimum coagulant dosage. This is supported by the study of Muhammad et al (2015) who use watermelon seed show that recommended ratio for the best mixtures of coagulants is at 80% of natural coagulant and 20% of...
artificial coagulant [6]. Results also proved that the higher the amount of natural coagulants used, the higher the turbidity reduction. This is proved by other study, Al-Mamun and Basir (2016) who found that the higher the amount of white propinac used, the higher the reduction in the turbidity. [7]. However, the turbidity removal using single watermelon rind is not efficient as proved in the study at W100, the removal is the lowest where it is only 48% in synthetic wastewater and 18% in the natural wastewater. Muhammad also found the similar trend using watermelon seed where the reduction also the lowest when watermelon seed used alone [4]. Addition of alum as artificial coagulant increases the effectiveness of watermelon rind as coagulant.

3.2. The pH

Figure 2 shows the initial and final pH in the natural and synthetic wastewater, before conducting the jar test and after one hour of settling time, respectively. The results for the pH value were compared with WHO standards. The pH reading will be varying at different temperature and condition of surrounding. A solution is acidic when the hydrogen ion, H⁺ is excess over hydroxide ion, OH⁻ while a solution was considered alkaline when the OH⁻ is at excess over H⁺ ion. Thus, any solution at pH of 0 to 7 is considered acidic and those within the pH range of 8 to 1 is considered as alkaline. The standard pH values according to the WHO standards for drinking water is at 6.5 to 8 [1]. The initial pH reading for the synthetic wastewater was taken before the jar test takes place while the final pH reading was taken one hour after the settling time in the same way study by Saravanan et al. [18]. Results show that all solution show an acidic solution before and after the experiment except the control sample reached the WHO drinking water standard. Initially, the A100 is the most acidic solution on contrary the final reading show that the WR70A30 is the most acidic. The lowest pH value of 100% of alum was also proved in the study by Ugwu et al. (2017) [4]. Comparing between synthetic and natural wastewater, the natural wastewater had higher pH or more alkaline than the synthetic wastewater. Initially, the pH reading for all natural wastewater were within the range of WHO standards [4]. The acidic results for the pH value in the synthetic wastewater may be affected by the acidic properties of the Benonite clay used. However, it did affect the performance of the watermelon rind to neutralize the pH of the water. Meanwhile, the initial pH reading of the natural wastewater was within the WHO standards indicate that water sources from the lake where the natural wastewater was not polluted and when treated with coagulant, it still met the WHO standards.

3.3. Fourier Transformed Infrared Spectroscopy (FTIR)

Figure 4 show a typical FTIR spectrum of untreated watermelon rind, treated with nitric acid and loaded with coagulant. FTIR spectra displayed several peaks that pertaining to different functional groups and the type of bonds of the compounds in WR [19]. This group was proved by the chemical structure of WR as shown in Figure 3. The results show that the observed spectra of WR loaded with coagulant and treated with acid have similar trend of peaks. The major functional groups present on WR were presented in Table 3. Among these spectra, the shifts in peaks of WR attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl groups are predominant contributors in coagulant uptake. The hydroxyl (OH) and carboxyl (COOH) peak ranged from 3300 to 2500 cm⁻¹ indicated functional groups in the watermelon rind. Previous study stated that these two functional groups are important in the coagulation process [17]. From observation, there is a strong shift in the OH peak that confirms the binding of WR ions with the floc. The coagulation ability of WR is most likely due to the presence of the carbohydrates which represent by the -C=O, -COO- asymmetric and -COO- symmetric. These functional groups will bind with the alkali and alkaline earth metals of coagulants that have positively charge. There was decreased peak intensity at 1709.25 cm⁻¹ in watermelon rind treated with nitric acid. These changes attributed possible disruptions of aliphatic and aromatic links, which were presented originally in untreated watermelon rind. Furthermore, there is no substantial peak shift observed for WR loaded with floc. This study proved that there is also binding of floc to the functional group.
Through this study, the WR coagulant were eventually similar in overall pattern due to dominant compounds are involved in the coagulant process.

![Figure 2](image_url) **Figure 2.** pH reading on (a) synthetic wastewater (b) natural wastewater.

| Functional groups                              | WR untreated | WR treated with HNO3 | WR loaded with coagulant |
|-----------------------------------------------|--------------|-----------------------|--------------------------|
| -OH stretching vibrations of acid groups      | 3279.59      | 3339.11               | 3336.42                  |
| -CH stretching vibrations of aldehyde groups  | 2917.87      | 2917.61               | 2918.58                  |
| -C=O stretching of carboxylic acids           | 1731.03      | 1709.25               | 1632.73                  |
| -COO- asymmetric vibration of ionic carboxylic groups | 1632.42 | 1637.31       | 1461.58                  |
| -COO- symmetric vibration of ionic carboxylic groups | 1379.19 | 1462.36       | 1369.08                  |

![Figure 3](image_url) **Figure 3.** Chemical structure of L-citrulline.
Figure 4. FT-IR spectra of WR (a) untreated, (b) treated with HNO3 and (c) loaded with coagulant.

4. Conclusion
It was concluded that the recommended ratio for the optimum dosage the treatment of wastewater using watermelon rind is at WR70A30. The highest turbidity reduction was recorded at 90% for WR70A30 in synthetic wastewater from 146 NTU to 15.2 NTU. Meanwhile, percentage reduction for turbidity in synthetic wastewater is at 72%, from 32.4 NTU to 9.09 NTU. The change of pH of the solution during the treatment is due to the addition of betonite clay, however it doesn't affect the result. It is also recommended that Bentonite clay can be replaced with another alternative to make synthetic wastewater since the Bentonite clay has an acidic property, which may affect the properties of the synthetic wastewater. The FTIR study also proved that the presence of OH and COOH which are involved during the turbidity removal. Studies on watermelon rind as a natural coagulant should be widened and improved due to its performance. In conclusion, watermelon rind is found to be effective in treating both natural and synthetic wastewater and can be an alternative to other natural coagulants to treat wastewater.

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