Removal of total suspended solid by natural coagulant derived from cassava peel waste

S Mohd-Asharuddin¹, N Othman¹, N S Mohd-Zin¹ and H A Tajaruñ²

¹ Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia.
² School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia.

Abstract. The present study was aimed to investigate the performance of starch derived from cassava peel waste as primary coagulant and coagulant aid. Comparable study was also conducted using commercially used aluminium sulfate (alum) as primary coagulant. A series of Jar tests were performed using raw water from Sembrong Barat water treatment plant. It was observed that coagulation test using cassava peel starch (CPS) alone had unappreciable removing ability. However, it was found that combination of alum-CPS successfully achieve up to 90.48% of total suspended solid (TSS) removal under optimized working conditions (pH 9, 7.5mg/L : 100 mg/L of alum : CPS dosage, rapid mixing of 200 rpm for 1 minute; 100 rpm for 2 minutes, slow mixing of 25 rpm for 30 minutes and 30 minutes settling time). This remarks the reduction in alum dosage up to 50% compared to coagulation test using alum alone. Therefore this finding suggesting that CPS can be considered as potential source of sustainable and effective coagulant aid for water treatment especially in developing countries.

1. Introduction
The speedy growing of human population worldwide and subsequent explosive increase in industrial growth and urbanization have steadily driving in growing volume of domestic and industrial effluent, agricultural waste and urban runoff that finally rest in the aquatic environment. This situation brings implication that water from either surface or ground sources are not safe for human consumption without undergoing a proper treatment regime. Adequate water treatment and disinfection are vital in eliminating water impurities including turbidity caused by the clay particles, colour due to decayed organic matter, algae, taste, odour, inorganic toxicants as well as microbial contaminants.

In developing countries, every year approximately 1.2 billion people do not have access to safe drinking water. Consumption of polluted water contributed to the death from diarrhea of more than six million people where 2 million of them are children [1]. The provision of clean water supply nearby for to support community daily needs will help in decreasing the health incidence with regards to skin diseases, eye infections as well as worm infections [2].

Many developing countries need to a high cost for imported chemicals such as aluminium salts, ferric salts and synthetic polymers as water treating agents. However, despite those highly effective chemical coagulants and disinfectants in reducing water turbidity and microbial contaminants, they are still lacking of important attribute of eco-friendliness that play an essential role for human health and ecosystem sustainability. The sludge formed from such treatment poses disposal problems with regards
to high aluminium content and tend to accumulate in the environment after being disposed. Recently, epidemiological, neuropathological and biochemical studies have assured the positive relation between prolong consumption of aluminium bearing water and Alzheimer disease [3]. Meanwhile, organic polymer such as acrylamide was observed to show neuro-toxicity and carcinogenic effect. Therefore, it is necessary to control the dosage of chemical coagulants in order to reduce residual chemicals in the treated water that subsequently brings in negative implication towards receiving bodies.

Recently, in attempt to reduce major shortcomings of using chemical coagulants, many efforts have been dedicated towards development of coagulants and coagulant aids from natural materials. Those materials that have been studied varied from animal and plant origin that includes the most prominent Moringa oleifera seed extracts, cactus mucilage, potatoram seed extracts, nirmali seed extracts, chitosan, chitin from exoskeleton of crustaceans, plant tannins, algal alginate as well as plants starches. For any natural materials to be developed into new coagulants or coagulant aids, it should be effective, renewable, locally and abundantly available, ecofriendly as well as economically viable.

In Malaysia, the habit of composting and waste recycling is not yet a widely adopted method and ultimately resorting to the easiest disposal method; landfilling. Close to 1000 million tonnes of agricultural waste are being generated internationally in a yearly basis and of this, about 1.2 million tonnes are being discarded into landfills in Malaysia alone [4]. The mishandling of fruit waste could be detrimental to the environment due to potential leaching into soil and water sources leading to further pollution [5].

In the production of crackers from cassava, the cassava tuber are usually peeled off to remove the outer layer that consist of the periderm, thin inner layer of cortex and some thin portion of the cortex. The peels are normally discarded and allowed to rot. Since the peels could make up 20-35% of the total weight of the cassava tuber, the conversion of these by-products into effective coagulant aid driven by intensive research study would increase their market value and ultimately benefits the producers. Kongkiattikajorn and Sornvoraweat [6] reported that cassava peels contain polysaccharides such as starch, pectin and holocellulose. It is well known that pectin, starch and cellulose containing abundant of carboxyl, hydroxyl and amino groups which has significant potential for metal sequestering [7]. Additionally, the functional groups bear effective charge to help alum forming larger flocs in coagulation and flocculation procees [8]. Our recent knowledge shows there is no literature describes the efficiency of cassava peel starch to remove TSS in dam water. So this study aimed to exploit starch from cassava peel waste as coagulant aid for the removal of TSS from raw water. The present work focuses on the optimization of main factors governing the process of coagulation-flocculation by natural materials namely pH, coagulant dosage and settling time.

2. Materials and method

2.1. Raw water sampling and characterization

A total of 4 samples of raw water will be collected once a week in a period of 4 weeks from raw water inlet tank at Sembrong Barat water treatment plant, Sembrong, Johor, Malaysia. The water samples were collected in 10L HDPE bottle. All sampling bottles were acid washed prior to sampling. Sample bottles were fully filled with water samples to ensure the elimination of air bubbles and organic particulate matter entrapped in the bottles. The samples were stored in an icebox and transported back to the lab for water characterization analysis. All samples were stored at 4°C before further analysis [9]. The water quality of the raw water is summarized in Table 1.
Table 1. Water quality characteristics of raw water from Sembrong Barat water treatment plant.

| Parameter          | Ex-situ study          | Mean         | INWQS Class |
|--------------------|------------------------|--------------|-------------|
|                    | Sample                 |              |             |
|                    | 1 (1/2/2017)           | 2 (15/2/2017)| 3 (1/3/2017)| 4 (15/3/2017)|              |
| Temperature (°C)   | 28.60                  | 29.10        | 28.90       | 28.70        | 28.83         | ─            |
| pH                 | 6.35                   | 6.75         | 7.20        | 7.07         | 6.84          | IIA           |
| Turbidity (NTU)    | 26.91                  | 21.60        | 27.41       | 28.32        | 26.06         | IIA           |
| Conductivity (µs/cm)| 166.00                | 176.00       | 165.00      | 169.00       | 169.00        | I             |
| DO (mg/L)          | 4.61                   | 5.42         | 4.23        | 4.59         | 4.71          | III           |
| COD (mg/L)         | 65.00                  | 46.00        | 53.00       | 52.00        | 54.00         | III           |
| BOD (mg/L)         | 2.89                   | 3.31         | 2.64        | 2.96         | 2.95          | IIA           |
| TDS (mg/L)         | 81.00                  | 76.00        | 89.00       | 97.00        | 85.75         | I             |
| TSS (mg/L)         | 22.00                  | 18.00        | 21.00       | 23.00        | 21.00         | I             |
| Ammonia (mg/L)     | 0.22                   | 0.18         | 0.26        | 0.32         | 0.25          | II            |
| Fe (mg/l)          | 0.71                   | 0.68         | 0.81        | 0.75         | 0.74          | I             |
| Mn (mg/l)          | 0.05                   | 0.04         | 0.05        | 0.05         | 0.05          | I             |

2.2. Preparation of cassava peel starch (CPS)

The cassava peels (CP) used in this study was obtained from Kilang Kerepek Ahmad Shah, Parit Raja, Johor, Malaysia. Qualified peels were selected and cleaned carefully using tap water before rinsed with distilled water. Then periderm layer was scrapped off from the whole peel using a fruit scraper. The peel then chopped into approximately 1 cm length and suspended in 2 times its volume of distilled water followed by pulverization in a domestic blender for 5 minutes. Subsequently, the pulp was suspended in 10 times of its volume of distilled water and stirred for 2 minutes. The suspension was then filtered using doubled fold muslin cloth. The filtrate was allowed to stand for 2 hours for sedimentation before the top liquid was decanted and discarded. The sediment was collected and sun dried for 12 hours to remove the moisture content. Dried CPS was kept in air tight plastic container for further use [10][11].

2.3. Characterization of CPS

2.3.1. Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX)

This analysis was conducted to determine the surface morphology and elemental distribution on the surface of the CPS samples. The samples were mounted on the copper stub using an adhesive carbon tape. Then the samples were sputtered with gold for 120 seconds at 30 mA under high vacuum until they were completely covered and ready to be used for the microscopic analysis. The SEM-EDX micrographs were observed using JEOL ISM-6380LA Field Emission Scanning Electron Microscope and JEOL Energy Dispersive X-Ray Spectrometer (USA).

2.3.2. Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectroscopy was done to identify surface functional group of CPS samples and performed using Perkin Elmer Spectrum 100. The adsorption bands were recorded at characteristics wave numbers between 600 cm⁻¹ and 4,000 cm⁻¹.
2.4. Preparation of CPS stock solution

Stock solution of 1000mg/L for CPS was prepared by adding 1g of CPS powder into 1L of distilled water. The suspension will be stirred for 1 hour in order to ensure uniform mixing of the particles. Prior to coagulation test, the CPS stock solution will be diluted with distilled water into desired CPS dosage. The calculation for dilution of stock solution was done using the following equation:

\[ M_1 V_1 = M_2 V_2 \]

Where:
- \( M_1 \) = initial stock solution concentration
- \( V_1 \) = volume of solution required
- \( M_2 \) = concentration of solution to be produced
- \( V_2 \) = volume of solution to be produced

2.5. Preparation of alum stock solution

Analytical grade of commercial alum, Aluminium sulfate (Al\(_2\)(SO\(_4\))\(_3\).18H\(_2\)O (Merck) was used in this study. Alum solution of 5 g/L was prepared by dissolving the alum in deionized water. Further dilutions from this stock solution were performed in order to obtain desired alum concentrations.

2.6. Optimization study using Jar test

Standard jar tests were conducted at room temperature (25±1°C) using conventional 6 paddles flocculator (Velp, Italy). 6 beakers of 1000ml in volume were filled with 1000ml of raw water samples. Adjustment of pH was done using 0.1 M hydrochloric acid (HCl) (Merck) and 0.1 M sodium hydroxide (NaOH)(Merck).

Three optimization studies were conducted consist of i) alum as coagulant; ii) CPS as coagulant; iii) Combination coagulant of alum-CPS. For combination coagulant experiment, alum as the primary coagulant were added initially at the start of the rapid mixing phase, followed by addition of CPS after 30 second. Each study was conducted in three stages with different working conditions as tabulated in Table 2. Other experimental conditions were kept constant: Rapid mixing (200 rpm for 1 minute; 100 rpm for 2 minutes), slow mixing (25 rpm for 30 minutes) [12].

| Stage | Coagulant | pH | Coagulant dosage (mg/l) | Settling time (min) | References |
|-------|-----------|----|------------------------|--------------------|------------|
| 1     | Alum      | 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 | 5, 10, 15, 20, 25, 30 | 10, 20, 30, 60, 90, 120 | [12][13][14] |
| 2     | CPS       | 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 | 100, 200, 300, 400, 500, 600 | 10, 20, 30, 60, 90, 121 |           |
| 3     | Alum-CPS  | 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 | 50%, 70%, 100% | 10, 20, 30, 60, 90, 122 |           |

Upon the completion of Jar test, supernatant samples were withdraw from 2 cm below the surface level and analyzed for residual TSS and turbidity in accordance with the standard method [9]. A DR6000 Hach spectrophotometer was used to determine TSS while turbidity measurement was performed using Hach turbidity meter. The removal efficiency for each parameter analysis was calculated based on Eq. (2):
Removal (%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \tag{2}

Where:

\( C_i \) = initial concentration of the sample
\( C_f \) = final concentration of the sample

3. Results and Discussion

3.1. Characterization of cassava peel starch (CPS)

SEM micrograph at x500 magnification of native CPS (Figure 1) indicates the non-porous characteristic with appearance of numerous starch granules in smooth and globular shape, whereas EDX spectrum (Figure 2) shows characteristic signal of Na, Ca and Si which attributed to metal binding property [15]. This observation is in parallel with other studies using cassava peel [16][17]. Recent work shows 80% of amylopectin and 20% of amylose are deposited in the starch granule of cassava peel [10]. A research on unmodified starch-based coagulant evidenced that starch enhances the sequestering of positive charged metal ions which tends to destabilize the metal and subsequently forming agglomerates and precipitate [18].

The FTIR spectrum pattern is depicted in Figure 3. The spectrum displays a number of peaks that indicates the functional groups available on the surface of CPS. The broad peak between 3500-3000 cm\(^{-1}\) is assigned to –NH and bounded –OH groups. The band at 2926 cm\(^{-1}\) is regards to stretching vibration of –CH\(_2\) and –CH\(_3\) groups. Whereas bending vibration appeared at 1610 cm\(^{-1}\) corresponds to stretching of carboxylate and carboxyl groups. Band position noted at 1331 cm\(^{-1}\) is indicative of stretching vibration of ionic carboxylic group while deep band at 1009 cm\(^{-1}\) represents the stretching of carbonyl and bending of hydroxyl groups. The appearance of amino, hydroxyl and carboxyl group is appreciable since those groups are referred to be important for flocculation process [19].
3.2. Optimization studies

3.2.1. Effect of pH

The pH of the solution plays a major role behind the process of coagulation and flocculation by affecting the surface charge of the coagulants and stabilization of the suspension [20]. Based on Figure 4, it was observed that highest removal of TSS was achieved at pH 7, pH 2 and pH 9 respectively for alum, CPS and alum-CPS. Same observation was reported by a study using rice flour where acidic environment if more favorable for TSS removal [21]. Wongasongsup [22] described that at acidic environment, lone electron pair of nitrogen of amino group residing on the surface of starch granular became protonated and became positively charged meanwhile the carboxyl group became neutral.

3.2.2. Effect of coagulant dosage

Figure 5 and 6 indicates the recommended dosage to achieve the highest removal of TSS using alum alone (83.33%) and CPS (42.59%) is 15mg/L and 200 mg/L respectively. This study showed that removal of TSS was proportionate to the increasing dosage of alum. Chee [21] stated that sweep flocculation and charge neutralization are the two main mechanisms that governing the coagulation process using alum. The increasing dosage of alum causing more suspended particles enmeshed in the hydroxide precipitate which leading to higher TSS removal. Similarly to alum, addition of more CPS has improving the TSS removal, however increasing addition of the natural polymer beyond the optimum point causing reduction in the removal of TSS which this situation could be subjected to surface saturation by excessive quantity of polymer particles that results in particle restabilization [23].
As can be seen in Figure 7, addition of CPS as coagulant aid has efficiently increased the TSS removal up to 90.48% with lower dosage ratio of alum:CPS (7.5 mg/L : 100 mg/L of alum : CPS). This observation could be due to the reduction of surface area coverage necessary for polymer bridging to establish. This situation promotes the formation of large initial flocs when pollutant particles were encapsulated with aluminium hydroxo complexes during the addition of alum in the initial stage [24].

Figure 5. Effect of varying alum dosage on TSS removal (initial pH = 7; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3)

Figure 6. Effect of varying CPS dosage on TSS removal (initial pH = 7; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3)

Figure 7. Effect of varying alum-CPS dosage on TSS removal (initial pH = 7; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3)

3.2.3. Effect of settling time
Figure 8 shows recommended settling time was 60 minutes and 20 minutes respectively for alum and CPS alone with TSS removal of 84.06% (alum) and 23.19% (CPS). It was also found that recommended settling time was 30 minutes for combination of alum and CPS. Faster settling speed of alum aided by CPS was suggested due to attachment of high molecular weight of CPS polymer chain onto initial flocs form by primary addition of alum [21].
4. Conclusion
This study demonstrates that an effective coagulant aid can be obtained from cassava peel waste. The use of unmodified CPS as coagulant aid in the treatment of raw water showed positive result and successfully reduce up to 50% dosage of commercially used alum. Under recommended working conditions (pH 9, 7.5mg/L : 100 mg/L of alum : CPS dosage, rapid mixing of 200 rpm for 1 minute; 100 rpm for 2 minutes, slow mixing of 25 rpm for 30 minutes and 30 minutes settling time), combination of alum:CPS yielded high removal of TSS up 90.48%. The present study proven the potential of CPS as promising natural coagulant aid in reducing harmful inorganic coagulants such as alum in coagulation process for water treatment plants. Further research could be performed on modification of CPS to challenge the efficiency of this natural material to the maximum.

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