

Performance Assessment of Cassava Peel Starch and Alum as Dual Coagulant for Turbidity Removal in Dam Water

Syazwani Mohd Asharuddin¹, Norzila Othman^{1,*}, Nur Shaylinda Mohd Zin¹,
Husnul Azan Tajarudin², Mohd Fadhil Md. Din³, Vicky Kumar¹

¹Faculty of Civil and Environmental Engineering,
Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, MALAYSIA.

²School of Industrial Technology,
Universiti Sains Malaysia, 11800, Penang, MALAYSIA.

³Faculty of Civil Engineering,
Universiti Teknologi Malaysia, 81310 Skudai, Johor, MALAYSIA.

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Abstract: The agricultural and food processing industries generate a significant portion of residues, refuse and waste. Conversion of these wastes into useful end product would be beneficial not only to the economy but also the environment as it reducing the solid waste disposal problem. The present study was aimed to investigate the performance of cassava peel starch (CPS) extracted from cassava peel waste in combination with alum to act as dual coagulant for turbidity removal in raw water from Sembrong dam. Comparative studies by employing both alum and CPS as primary coagulant using several series of Jar test were also conducted. Results showed that the usage of alum-CPS as dual coagulant not only enhanced the turbidity removal with maximum achievement up to 91.47%, but also significantly improve the coagulation process by reducing both alum dosage and settling time up to 50% which indicates broad prospects to be further developed as emerging green coagulant.

Keywords: coagulation, flocculation, dual coagulant, alum, cassava peel, starch

1. Introduction

Coagulation and flocculation has remained the most prominent method for the removal of colloidal particles and organic matter in water and wastewater treatments for several decades. The process is generally initiated by adding coagulant agent to react with the particles in the water to form hydrophobic hydroxide and polymeric compounds [1]. The coagulant interaction with colloidal materials is commonly expressed in two different mechanisms known as charge neutralization and sweep flocculation [2]. Under correct coagulant dosage and pH, destabilization of negatively charged colloidal particles in water could be achieved by the addition of cationic salts. Consequently, the destabilized particles adhere to one another and forming solids known as flocs. However, when excessive amount of coagulant is added, charge reversal may take place where the destabilized particles will be restabilized. In another condition where water pH is nearly neutral, formation of amorphous hydroxide precipitate could occur due to limited solubility of Al (III) and Fe (III). This growing precipitate

tends to trap the colloidal particles which contribute to effective removal of impurities through sweep flocculation mechanism [2].

Conventionally, cationic salts such as aluminium chloride, aluminium sulfate, ferric chloride, ferric sulfate as well as polyaluminium chloride are typically used as the primary coagulants in most developed countries. However recent studies have discovered a number of drawbacks with regards to the usage of alum salts such as the onset of Alzheimer's disease and some other related health effects associated with alum residue in treated waters [3]. Moreover, there is also problem of alum disadvantage due to alum reaction towards natural alkalinity of water which results in pH reduction [4].

Owing to the inherent drawbacks engaged with the adoption of chemical coagulants, recently many attention have been given to the use of natural biomass as coagulant aid that effectively facilitating water clarification process. The usage of effective coagulant aid not only reducing the dosage of chemical coagulants which in turns eliminate residual monomers from treatment process and reaction by-products. Some of the

coagulant aid of natural origin that have been studied include snail shell [3], lignin and tannin [4], rice starch [5], cactus mucilage [6], as well as fruit seeds [7] – [11].

In the present study, starch derived from cassava peel is being proposed as a low cost material to aid alum for turbidity removal in dam water. Starch is considered as high performance natural polymeric material that plays a special role in water purification in which it can be obtained at lower price compared to other natural polymers such as tannins [12] and chitosan [13]. The presence of active agents in starch has been linked to the observation of water clarification effects by numerous studies that extracting starch from various plants [14] [15]. Starch is composed by combination of anhydroglucose units namely amylose and amylopectin (Fig. 1). Amylose exhibits linear assembly of glucose monomers connected through α -1, 4-glycosidic bonds. While amylopectin with about 5–6% branches is the major molecular component of cassava starch.

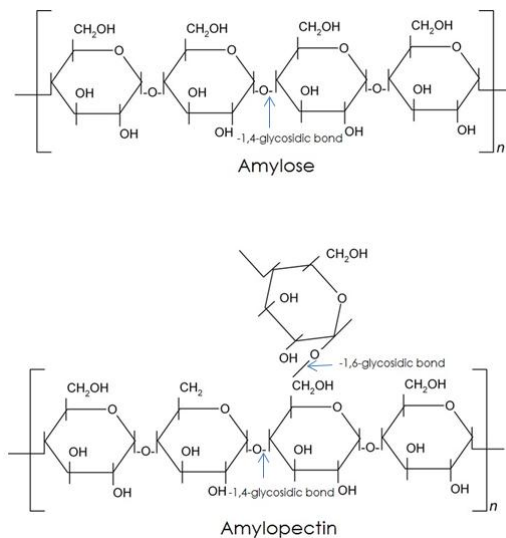


Fig. 1 Chemical structure of amylose and amylopectin.

Cassava is cultivated mainly for starch and it plays a major role as carbohydrate source numerous people in many regions. During the processing of cassava, the roots outer layer known as periderms are normally peeled off. The peels generally consist of a thin brown outer covering which attached to a thicker parenchymatous inner covering. Kongkiattikajorn & Sornvoraweat [16] stated that the peel constitute about 10-12% of the total dry matter of the root and account for 20-35% of the weight of the tuber. Therefore, every year, a generous amount of cassava peel waste is discarded into the environment by the food processing industries as the peels are inedible and lack of commercial value. Hence, this study aimed to convert the waste biomass into value added coagulant aid using starch extracted from cassava peel waste. The experimental works were performed using alum as primary coagulant, cassava peel starch (CPS) as primary coagulant and combination of alum-

CPS. It was expected that the high constituents of hydroxyl and carboxyl groups in the starch polymer could serves as binding site for metallic cations that in later stage inducing flocculation process to take place.

2. Materials and Methods

2.1 Preparation of Starch

Cassava peel (Fig. 2) was collected from local cassava chips factory (Kilang Kerepek Mad Shah dan Asiah) located at Parit Raja Darat, Johor, Malaysia. The starch extraction procedure was done according to Benesi [17] and Kokasih et al. [18] with slight modification where the starch was originally extracted from cassava peel waste. Initially, good qualities of peels were selected and washed using tap water repeatedly to remove any surface impurities. The peels were further processed by removing the woody outer layer using a fruit scrapper. The peel then cut into 1cm in length and suspended in double amount of its volume of distilled water. Later the suspension was pulverized using a domestic blender for 5 minutes. The mixture was filtered through double fold muslin cloth followed by sedimentation process for at least 2 hours. Finally, the top liquid then discarded while the white sediment was collected and dried under the sun for 12 hours until it reached constant weight to ensure entire removal of moisture content. Dried CPS (Fig. 3) was stored in an air tight plastic container for further experimental used.



Fig. 2 Raw cassava peel.



Fig. 3 Dried CPS.

2.2 Stock solutions and suspensions

The CPS powder (1 g) was firstly suspended in 1000 mL of distilled water. The suspension was then stirred for 60 minutes to ensure uniform mixing of the particles. Prior to jar test, these stock solution was further diluted with appropriate volume of distilled water to obtain desired CPS dosage.

Aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) (Merck) of analytical grade was employed in this study. 5 g of alum was dissolved in distilled water and then diluted with distilled water to achieve intended concentrations.

In ensuring the consistency and replication throughout the treatment regimes, stock solutions were prepared for coagulant dosing. Dilution of stock solution was performed using the following equation:

$$M_1V_1 = M_2V_2 \quad (1)$$

Where:

M_1 = initial stock solution concentration (mg/L)

V_1 = volume of stock solution required (L)

M_2 = concentration of solution to be produced (mg/L)

V_2 = volume of solution to be produced (L)

2.3 Water samples

Water samples were obtained from intake tank at Sembrong Barat water treatment plant, Sembrong, Johor, Malaysia. All samples were kept in acid washed HDPE bottles. All sampling technique, sample storage and water characterization analysis were performed according to standard method by APHA [19]. The average of main parameters analyzed is shown in Table 1.

Table 1 Quality parameters of Sembrong dam raw water.

Parameter	Average reading
Temperature (°C)	28.82
pH	6.84
Turbidity (NTU)	26.06
Conductivity ($\mu\text{s}/\text{cm}$)	169.00
DO (mg/L)	4.71
COD (mg/L)	54.00
BOD (mg/L)	2.95
TDS (mg/L)	85.75
TSS (mg/L)	21.00
Ammonia (mg/L)	0.25
Fe (mg/L)	0.74
Mn (mg/L)	0.05

2.4 Coagulation and flocculation studies

Standard flocculator equipped with 6 paddles (Velp, Italy) was employed in this study. All 6 beakers were filled with 1000 mL of water samples. The pH of water samples were measured using portable pH meter (Hanna).

pH adjustment was done using 0.1 M hydrochloric acid (Merck) and 0.1 M sodium hydroxide (Merck). Optimization studies were performed under three sets of experimental conditions: i) alum as primary coagulant ii) CPS as primary coagulant iii) combination of alum-CPS. When alum-CPS combination was used, the CPS was added only after 30 seconds alum was added [20]. All parameters subjected to optimization studies and the working ranges used are summarized in Table 2.

For each Jar test performed, rapid stirring period was set for 1 minute at 200 rpm followed by 2 minutes at 100 rpm. Subsequently, slow stirring period was conducted for 30 minutes at reduced speed of 25 rpm. Upon completion of settling time, water samples were collected at 2 cm below the surface level. Turbidity measurement was done using Hach handheld turbidity meter. The percentage of removal was calculated according to the equation as below:

$$\text{Removal}(\%) = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (2)$$

Where:

C_i = initial turbidity of the sample

C_f = final turbidity of the sample

Table 2 Experimental range for optimization study.

Parameter	Coagulant		
	Alum	CPS	Alum-CPS
pH	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	2, 3, 4, 5, 6, 7, 8, 9, 10, 11
Coagulant dosage (mg/L)	5, 10, 15, 20, 25, 30	100, 200, 300, 400, 500, 600	100%:0%, 70%:30%, 50%:50%, 30%:70%, 0%:100%
Slow mixing speed (rpm)	0, 10, 20, 30, 40, 50	0, 10, 20, 30, 40, 50	0, 10, 20, 30, 40, 50
Slow mixing time (min)	0, 5, 10, 15, 20, 25, 30	0, 5, 10, 15, 20, 25, 30	0, 5, 10, 15, 20, 25, 30
Settling time (min)	10, 20, 30, 60, 90, 120	10, 20, 30, 60, 90, 121	10, 20, 30, 60, 90, 122

3. Results and Discussion

Three sets of experimental conditions were performed to study the effect of both alum and CPS as primary coagulant and combination of alum-CPS as dual coagulant in removal of turbidity in raw water samples.

3.1 Effect of varying alum dosage as primary coagulant

It is well known that coagulation activity is highly affected by the dosage of coagulant and bivalent cationic species [21]. The result obtained from this study is

expressed in percentage as shown in Fig. 4. The highest removal of turbidity (85.20%) was recorded for alum dosage of 15 mg/L. It was noted that increasing alum dosage seems to enhance turbidity removal due to higher amount of floc formation. Conversely, further increment of alum dosage beyond 15 mg/L does not appear to be beneficial for turbidity removal which indicates restabilization of colloidal particles due to charge reversal [22] – [24]. This finding is in agreement with other studies on that reported the turbidity removal was decreased when coagulant was added in a greater dosage than the optimal concentration [5][25]. Therefore precise control on coagulant dosing should be considered in water treatment to achieve optimum turbidity removal.

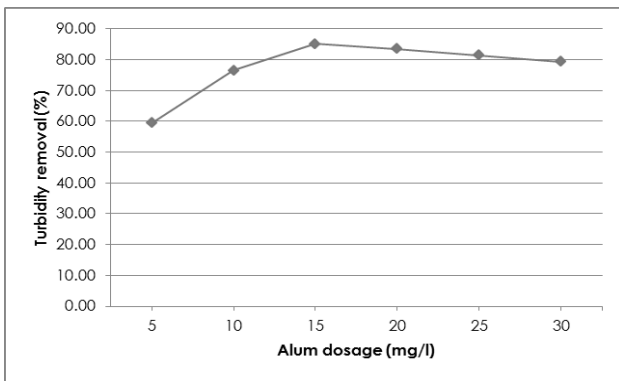


Fig. 4 Effect of alum dosage on turbidity removal (initial pH = 7; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3).

3.2 Effect of varying CPS dosage as primary coagulant

The result obtained from this study using CPS as primary coagulant is depicted in Fig. 5. From the result, maximum turbidity removal of 29.20% was achieved at 200 mg/L of CPS dosage. It was observed that the increase in CPS dosage above one point (< 200 mg/L) resulting reduction of turbidity removal. This situation most likely caused by difficult coulombic attraction to occur between CPS and colloidal particles in the water due to ionization product of both CPS and colloidal particles are negatively charged, hence both particles repelled from each other. Devrimci et al. [25] stated that the low concentration of positively charged ions of the coagulant might not sufficient enough in neutralizing the colloidal surfaces to achieve optimal coagulation.

Similar observation was indicated by a study using sago starch [26]. The study justify that the starch present in the form of anionic polymer, hence further addition of negative ions into the water does not reduce the surface charge but rather improves the stability of the colloids. Nonetheless, the study further elaborate that the removal of cationic metal ions were enhanced with the addition of sago starch. The removal of cationic metals from aqueous solution could happen through several mechanisms including ion exchange and complexation by metal

chelating agents constitute on the surface of the polymer [27][28]. It can be related to the previous study on abundance presence of negative charged functional groups such as carboxylic acid and hydroxyl group that would promote the metal ion binding [29][30]. Since starch is reported to have high molecular weight (~0.82–2.5 × 10⁸ g/mol), the complex of starch-metal ion would further precipitate that results in a slight reduction of turbidity [8].

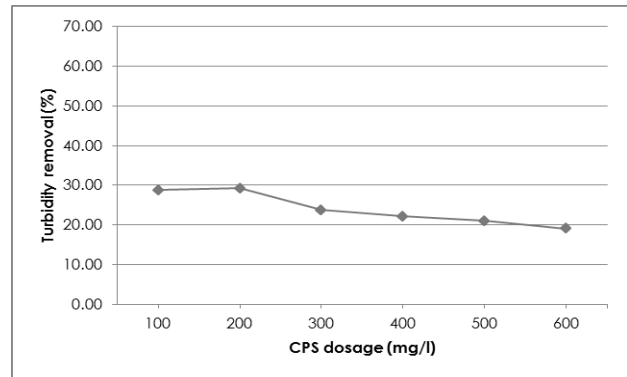


Fig. 5 Effect of CPS dosage on turbidity removal (initial pH = 7; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3).

3.3 Effect of varying alum-CPS dosage as dual coagulant

In comparison to Fig. 4 and Fig. 5, the result illustrated in Fig. 6 and visual observation as in Fig.7 indicates that the removal of turbidity was further enhanced when alum is used in combination with the coagulant aid of CPS. The maximum turbidity removal was achieved up to 90.32% at combination ratio alum:CPS of 50%:50% which equivalent to 7.5 mg/L : 100 mg/l of alum:CPS. The study also demonstrated that turbidity removal was increase with the reduction of alum from 100% to 50%; and with the increase of CPS from 0% to 50%.

According to Abiola [31], the interaction established between cationic charges of Al³⁺ with anionic charge of starch molecules produces insoluble aluminium salts. The insoluble salts are expected to initiate the formation of micro flocs at the initial stage which in later stage, it's gradually developing into larger flocs and finally get settled [32]. The enhanced turbidity removal with the presence of CPS could also be linked to the findings reported by Mavura et al. [14]. Comparable to starch, *Maerua subcordata* plant extract indicated very high content of amylopectin. The study deduces that amylopectin could be the chief agent in enhancing water clarity through formation of bridges between the particles, consequently increasing the colloidal mass which leads to precipitation.

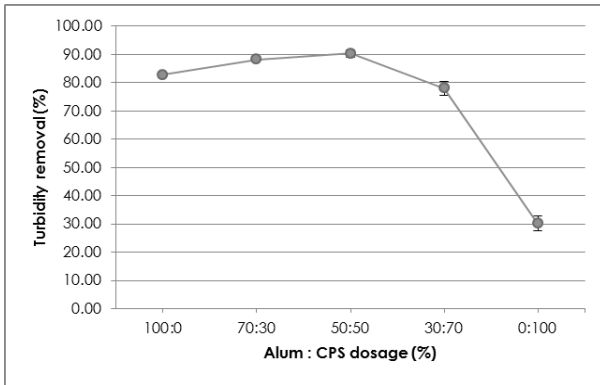


Fig. 6 Effect of alum-CPS dosage on turbidity removal (initial pH = 7; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3).

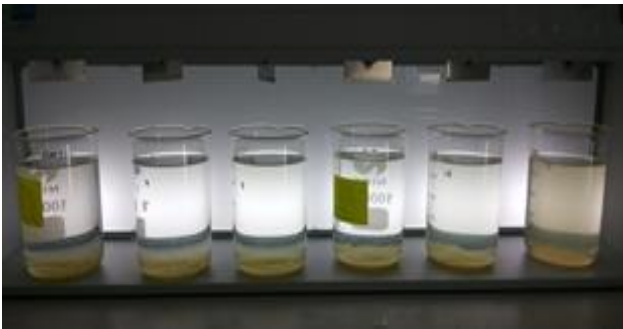


Fig. 7 Treated water after coagulation test on the effect of varying combination of alum-CPS dosage

3.4 Effect of pH on turbidity removal

Based on Fig. 8, results showed that the removal of turbidity by alum-CPS requires initial pH of 9 as compared to the treatment using alum alone (pH 7) and CPS alone (pH 2). These results are sufficiently in accordance with other studies that mentioned higher pH values are optimal for natural coagulants including *M. oleifera*, *P.juliflora*, *C.latifaria*, chestnut and oak acorn [21][25][31]. Many researchers stipulate that alum solubility is depending on the pH and most optimum between pH 5 and 7.5. Beyond this range, coagulation activity using alum salts is retarded [1][2].

Okuda et al. [24] asserted that bivalent cations from aqua medium could be attracted to negative charged active compounds resides on the surface of the biomass which subsequently forming a net-like structure which enmeshed the colloidal particles and remove it from water via sweep flocculation. Whereas Oladoja [3] inferred that natural coagulant that is abundant with anionic active components could serve as the reservoir of alkalinity and facilitate the neutralization of the acid produced from the hydrolysis of aluminium ions. In natural environment, the hydrolyzation of aluminium ion causes the reduction in pH in the treated water. Therefore, hydrated lime is frequently used in water treatment to neutralize the pH of treated water. Therefore, as obtained from the present

study, initial pH of 9 required for optimum removal of turbidity by alum-CPS can be considered as an advantage that create ample environment for floc formation as well as producing neutral pH of treated water.

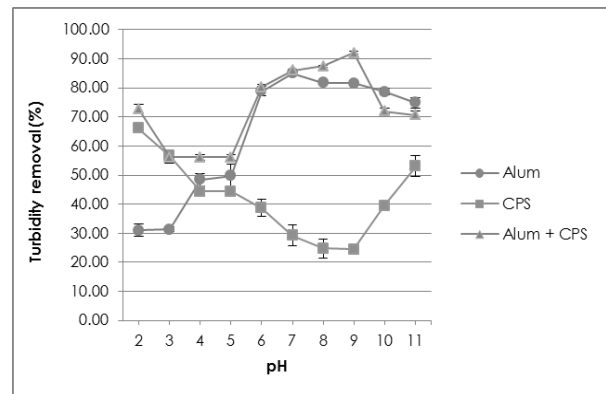


Fig. 8 Effect of pH on turbidity removal (alum= 15 mg/l; CPS= 200 mg/l; alum-CPS = 7mg/L-100 mg/l ; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 25 rpm-30 min, settling time 60 min; n = 3).

3.5 Effect of slow mixing speed on turbidity removal

The effect of slow mixing speed was considered to be explored by varying the velocity from 0 to 50 rpm. The present study indicated that the highest turbidity removal of 90.01% and 86.19% for both alum-CPS and alum alone respectively was obtained at velocity of slow mixing of 10 rpm (Fig. 9). Significant difference in percentage of turbidity removal was noted when the velocity was elevated from 0 rpm to 10 rpm which this condition recommend that slow mixing is a crucial step in enhancing the growth of flocs ($p < 0.05$). From the observation, it was also noted that, at higher velocity of slow mixing (> 20 rpm) causing significant drops in turbidity removal of all coagulant ($P < 0.05$). This could be occur due to disruptive forces that resulting floc breakage and reduction of effective particles collision in a shear field caused by increasing particle size [33].

The settings for mixing phase play a very significant role in attaining high turbidity removal in treated water. At the early stage of coagulation and flocculation process, rapid mixing is performed to induce uniform dispersion of coagulant in the suspension. At this stage, destabilization reaction takes place and primary flocs are formed [1][3]. In the following stage of slow mixing, the floc particles are allowed to collide between one another to form aggregates which will develop in size and density before get settled [22]. Several study reported the changes in rapid mixing conditions result in insignificant effect on turbidity removal [34].

Apart from retaining growing flocs in the suspension, slow mixing promotes reformation of aggregates, association of metal cations onto functional groups and ligands, as well as bindings of organic matter onto the coagulant [35].

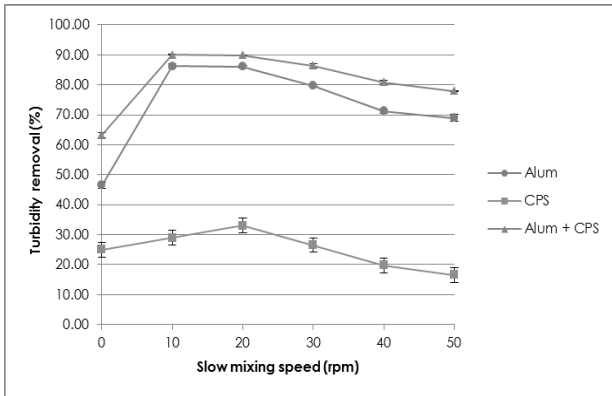


Fig. 9 Effect of slow mixing speed on turbidity removal (alum= 15 mg/l; CPS= 200 mg/l; alum-CPS = 7mg/L-100 mg/l; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing time = 30 min; settling time = 30 min; n = 3).

3.6 Effect of settling time on turbidity removal

Settling time is among the paramount factors to be considered for coagulation and flocculation process as it influences the overall cost and efficiency of the coagulation process. The result as presented in Fig. 11, indicates that at optimized pH and dosage, increasing settling period from 10 to 30 minutes had significantly enhanced the removal of turbidity for alum-CPS with turbidity removal (85.90% to 91.47%). Further increase above 30 minutes would not result in significant increase in turbidity removal ($p > 0.05$).

Apart from that, it was also observed that the treatment using combination of alum-CPS yielded significantly higher removal of turbidity at any period as compared to the treatment using either alum alone or CPS alone ($P < 0.05$). Recommended settling time for treatment using alum alone was noted at settling time of 60 minute with 83.78% of turbidity removal while little increment of turbidity removal was observed for treatment using CPS alone when settling time was raised from 10 minutes to 120 minutes. A study reported that the high settling velocity as obtained in the treatment using alum-CPS is mostly like due to long structure of starch constituents which make it high in molecular weight. This characteristic enables the alum-starch complex to interact with more colloidal particles at the same time which leading to formation of bigger and denser flocs that can settle faster [36].

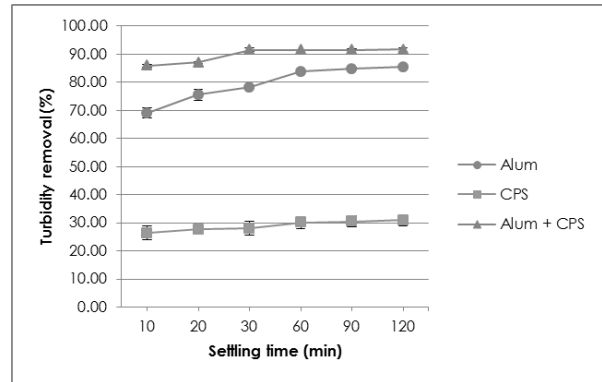


Fig. 11 Effect of settling time on turbidity removal (alum= 15 mg/l; CPS= 200 mg/l; alum-CPS = 7mg/L-100 mg/l ; rapid-mixing = 200 rpm-1 min, 100 rpm-2 min; slow-mixing = 10 rpm- 30 min; n = 3).

4. Summary

The results obtained from optimization study confirm the positive coagulation potential of the investigated natural coagulant that was extracted from agricultural waste material. The treatment using the combination of alum-CPS have achieved up to 91.47% of turbidity removal by employing the optimized conditions of pH 9, 7.5mg/L of alum dosage, aided by 100 mg/L of CPS dosage, rapid mixing of 200 rpm for 1 minutes, followed by 10 rpm for 10 minutes, and settling time of 30 minutes. As compared to the treatment using alum alone, the addition of 100mg/L of CPS has successfully reducing 50% of alum dosage with highest percentage of turbidity removal. This suggests that the cassava peel starch has the potential to be developed into new coagulant and provides a good source of natural coagulant in complementary geographical areas.

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