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ORIGINAL ARTICLE

The Effect of Silane Treatment on Nanosized *Carica Papaya* Seed Modified Pullulan as Biocoagulant in Wastewater Treatment

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KEYWORDS

Biocoagulant;

Wastewater treatment;

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ABSTRACT: Currently, conventional wastewater treatment process used chemical coagulant such as Aluminium sulphate. However, the residual aluminium in treated wastewater causes toxicity and serious health issues such as Alzheimer' disease. Thus, in this study the potential of nanosized *Carica Papaya* (CP) seeds treated by silane coupling agent incorporated to pullulan on wastewater treatment was investigated. The biocoagulant produce prepared at a different composition of CP range from 1% to 9% was used to treat sewage wastewater. The biocoagulant was characterized by particle size analyser, FTIR and FESEM. The treated wastewater was analyzed by jar test in term of turbidity, pH, dissolved oxygen and Total Suspended Solid with biocoagulant dosage at 0.6 g L^{-1}. The size of nanosized biocoagulant was obtained at 608.9 nm. Silane treatment provides well dispersion of nanosized *Carica Papaya* seed powder in the pullulan matrix phase. FTIR analysis shows the presence of O-H, C=O and Si-O-CH_3 bond. The highest turbidity reduction observed at the composition of nanosized CP5/P and silane treated nanosized CP5/P up to 93.89% and 93.98% respectively. However, no significant changes observed on turbidity reduction with increasing CP seeds content for both biocoagulant. Further, at these compositions, the TSS reduced up to 20% and 60% respectively. The DO value of wastewater decreased from the initial value and the increased the pH from 6.58 to 6.69 lead to the neutral condition. Therefore, the effectiveness of both untreated and silane treated biocoagulant were further confirmed upon textile wastewater with turbidity reduction achieved up to 7.84% and 14.54 % respectively. Overall, silane treatment enhanced the effectiveness of nanosized CP modified pullulan as biocoagulant.

INTRODUCTION

Nowadays, one of the biggest challenges to sustain the modern society is to maintain the good water quality. Water pollution is becoming serious limiting factor for maintaining the good water quality in many countries. The factors of water pollution are the discharge of industrial waste and sewage from rural areas [1]. The pollutants that come from household and industries such as heavy metals, chemical compounds and toxic substances become harder to eliminate due to the solubility in water which consequently affect in turbidity increment[2].

Coagulation plays an important role in water and wastewater treatment to control the particulates, microorganisms, natural and synthetic organic matter [3]. The coagulation process is contributing to energy saving, and easily control treatment alternative [4]. Coagulation process widely used because of its easy operation, simple design and low energy consumption [5]. In addition, coagulation also effective in precipitation of particle, removing pathogens and reduce the turbidity of water.

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Aluminium polychloride and aluminium sulphate (alum) are the chemical based-coagulant used in coagulation process[6]. Previous study was found the used of alum in treated water causes toxicity and serious health issues such as Alzheimer' disease due to the high concentration of residual alum[4]. Therefore, coagulation aid was needed by conventional coagulant such as alum to excellently treat water with high turbidity[7].

These scenarios have attracted many researchers to explore on potential of natural coagulant such as *Carica Papaya* seed and *Moringa Oleifera* for wastewater treatment application [3]. *Carica Papaya* (CP) is which abundantly available in Malaysia was proven effectively act as natural coagulant [8]. It was reported that the papaya seed powders are able to reduce turbidity up to 89.14% at optimum dosage of 0.6 g L^{-1}[1]. According to Hezarkhani [9], pullulan is non plant-based coagulant which is degradable polysaccharide with molecular formula (C6H10O5)n. Pullulan has excellent water solubility, adhesive properties and capability to form fibers and films[10]. Pullulan was successfully act as coagulant. However, limited study was found on the effect of silane treatment on CP seeds upon wastewater treatment application. Therefore, the effectiveness of biocoagulant on turbidity, pH, DO and TSS were investigated.

Literature review

Coagulation in wastewater treatment

Coagulation is the process used in wastewater treatment involve added the small particles into larger aggregates which is known as flocs and for adsorbing dissolved organic matter on to particulate aggregates to remove impurities from solid or liquid separation process[3]. The aim of the coagulation process is to eliminate suspended colloidal particles and diminish turbidity in water [7]. The chemical-based coagulant or known as conventional coagulant usually used in wastewater treatment including the removal of dissolved chemical species and turbidity from water. The chemical based coagulant that commonly used is alum ($AlCl_3$), ferric chloride ($FeCl_3$) and polyaluminium chloride (PAC) [11]. However, these coagulants have disadvantages that is related to the wastewater treatment such as ineffective in water with low temperature, high cost since the coagulant is expensive, produce high volume of sludge and effect the pH of treated water. The usage of large amount of this coagulant continuously cause the health disease to the water consumers since the small amount of coagulant remain in the treated water [12]. Alum also cause the development of Alzheimer's disease in human. Thus, it is vital to substitute the usage of chemical based coagulant into the natural coagulant to provide safe environment.

Pullulan as biocoagulant

Pullulan is water-soluble microbial polysaccharides. Pullulan is one of the polymers produced by the black yeast fermentation medium like Aureobasidium pullulans[13]. It is perfect material for edible films and coatings as referring to its properties. Pullulan is abundance, renewable, biodegradability and biocompatibility to environment. The pullulan unique linkage pattern gives the polymer with unique physical properties such as good water solubility and consists of adhesive properties. Pullulan also have unique structure which consists of hydrophobic and hydrophilic characteristics [14]. The unique structure of pullulan enables it to be used in removing heavy metal in water due to it adhesive properties.

Carica Papaya seeds as biocoagulant

The usage of natural coagulant from plant based in water treatment have brought significant advantages. Firstly, it reduces the high cost of current water treatment system and not bring toxic effect since it is eco-friendly. Secondly, it is able to be used in the rural place with no facilities available for water treatment. Other than that, the residues form from the treatment process are not harmful the ecosystems and human being [15]. *Carica Papaya* seeds as natural coagulants have been discovered to provide high percentage reduction of turbidity and other residues compared to alum. It created a feasible, valuable, useful and robust product for water treatment. According to Unnisa [8], *Carica Papaya* seed significantly reduced turbidity up to 100% with no drops in pH value. Another study was reported that CP seed able to remove turbidity of river water with efficacy up to 89.14% and TSS removal was 90.29% at 0.6g L^{-1}. They claimed that CP seed work as coagulant due to the presence of the positively charged protein which bind to the negatively charged particles and enable the floc produced to settle and clear water is obtain[1].

The role of silane coupling agent as biocoagulant

Coupling agent plays an important role for enhancement of interfacial properties to improve surface properties like adhesion and wetting [16]. Silane coupling agent act as a bond or bridging agent to enhance the adhesion between an inorganic and organic substrate [17]. According to Balan[16], the modified coconut shell powder by silane coupling agent gives the good phase morphology, improved interfacial adhesion, increasing reinforcing efficiency and good mechanical properties of coconut shell powder. Others study on the effect of silane coupling agent on properties of biocomposites based on poly (lactic acid) and durian rind cellulose proved that the improvement of the interfacial between filler and matrix also leads to lower water uptake into biocomposites[17]. Coagulation process effectiveness is dependent on hydrophilic and hydrophobic properties of the coagulant. In sewage wastewater, there is possibility to have more distribution of natural organic matter with hydrophilic characteristics. Hydrophobicity is significant indicator to determine the biocoagulant is suitable to coagulate the particle inside wastewater.

MATERIALS AND METHODS

Preparation of Carica Papaya seed as biocoagulant

Carica Papaya seeds were removed from *Carica Papaya* fruit manually and then washed a few times with distilled water to remove impurities and dust. Next, the seeds were undergoing drying process at 60^0C for 48 hours. The seeds then crushed and sieved through a 300 µm and 150 µm siever. Nanosized particle was prepared by ball milling method. The milling process was done for 10 minutes in time interval 10s with 250 rpm. The biocoagulants were prepared at a different composition of *Carica Papaya* seed with and without silane coupling agent modified pullulan. The composition is shown in Tables 1 and 2. To prepare biocoagulant, 4g of pullulan was dissolved in 100ml distilled water. The mixture of CP and pullulan was maintained at 75-80 ^{0}C using hotplate stirrer and allow mixing well.

Table 1. Composition of nanosized *Carica Papaya* seed powder to pullulan.

Nanosized *Carica Papaya* seed powder (%)	Pullulan (%)	Designation
0	100	P100
1	99	CP1/P
3	97	CP3/P
5	95	CP5/P
7	93	CP7/P
9	91	CP9/P

Table 2. Composition of nanosized *Carica Papaya* seed treated with silane coupling agent to pullulan.

Nanosized *Carica Papaya* seed powder treated with silane coupling agent (%)	Pullulan (%)	Designation
0	100	P100
1	99	CP1/P
3	97	CP3/P
5	95	CP5/P
7	93	CP7/P
9	91	CP9/P

Preparation of nanosized Carica papaya seed powdertreated using silane coupling agent

Nanosized *Carica Papaya* seed powders were added in an ethanol/water (50/50, v/v) solution to form a suspension with a solid content of 20%, then the 3-aminopropyltrimethoxysilane (3% based on the *Carica Papaya* seed powder content) was added and the pH was adjusted to 4.5-5.0 by adding acetic acid to catalyse the hydrolysis of the trialoxysilane. Next, the suspension was kept under mechanical stirring for 3 hr to ensure the adsorption of the silane onto the nanosized *Carica Papaya* seed powder. Then, the modified CP seed was recovered by filtration and dried at 70 ^{0}C for 12 hr.

Characterization of the biocoagulant

Particle size analyser

The size of *Carica Papaya* seed powder was determined by using Particle size analyser. The 0.1g of *Carica Papaya* seed powder was dissolved in 100 ml of distilled water and mix to ensure it dispersed well. The sample was poured into cuvette and tested in particle size analyser to determine the nanosized of *Carica Papaya* seed powder.

Field Emission scanning electron microscopy

The surface morphology was characterized using Field emission scanning electron microscopy (FESEM). The size of samples was 1 cm x 1cm. All the samples were fixed to double-sided adhesive tape which is coated by a layer of conductive element which gold to avoid sample charging under the electron beam.

Infrared spectroscopy

The FTIR analysis will be performed using Agilent FTIR. The chemical modification of the *Carica papaya* seed powder incorporate to pullulan by with and without silane treatment will be monitored. The sample used is in liquid form with a high viscosity. The FTIR is work using Attenuated total reflection (ATR). ATR accessory operates by measuring the changes that occur in an internally reflected infrared beam when the beam comes into contact with a sample.

Analysis of the treated water quality in term of pH, Turbidity, Dissolved Oxygen (DO) and Total Suspended Solid (TSS)

The sample of wastewater to be tested was collected from surface of wastewater treatment plant at UTHM Parit Raja. Then, jar test method was use which includes six beakers where each beaker contains 1L of water sample. The biocoagulant was added according to the Table 1 and Table 2. The dosage used of biocoagulant used was fixed to 0.6 g L^{-1}. The samples were mix at 100 rpm for 1 minutes, then the speed was reduced to 50 rpm. The samples were allowed to mix for a period of 15 minutes. Next, the speed of mixing was reduced to 30 rpm for 10 minutes. The floc was allowed to settle at least for 20 minutes. 100 ml of the top of treated water of each beaker are taken for the determination of pH, turbidity, dissolved oxygen and Total Suspended Solid.

RESULTS AND DISCUSSIONS

Particle size analysis

The particle size of the *Carica Papaya* seed powder along with its polydispersity was identified using a particle size analyser. Table 3 summarizes the size of *Carica Papaya* seed powder below 10% (D10), median particle size (D50) and 90% of particle diameter (D90), based on particle size distribution result in Figure 1. Approximately, 10% of *Carica Papaya* seed powder was less than 313.3 nm. The median particle size is 437.4 nm. Almost 10% of the CP seeds obtained 6215 nm.

Table 3. Particle size of *Carica Papaya* seed powder.

Size Distribution	Particle Size (nm)		
	D_{10} [nm]	D_{50} [nm]	D_{90} [nm]
Intensity	313.3	437.4	6215

Figure 1 shows the characterization of *Carica Papaya* seed powder size in term of hydrodynamics diameter. The hydrodynamic diameter obtained was 608.9 nm. The hydrodynamic diameter indicates diameter of a hypothetical hard sphere that disperses with the same speed as the particle presence measured [18]. Based on the result obtained, the size of *Carica Papaya* seed powder is considered as nanosized particle. According to Hendrawati [12], the size of nanoparticle is considered from 1 to 1000 nanometers. From the results obtained, the polydispersity index of *Carica Papaya* seed powder is 0.217 which is less than 1 show that the nanosized *Carica Papaya* seed powder are uniform in size.

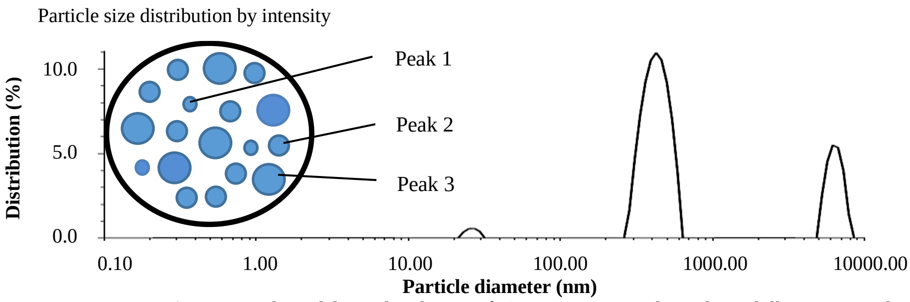

Figure 1. Multimodal size distribution of *Carica Papaya* seed powder and illustration on dispersion of multimodal size distributed.

FTIR analysis

Figure 2 shows the FTIR spectrum of pure pullulan, nanosized CP5/P biocoagulant and nanosized *Carica Papaya* seed powder. O-H stretching vibrations bond was observed at 3303 cm^{-1} for pullulan spectrum [9]. Next, the C-H vibrations appeared at 2925 cm^{-1}. The C-O stretching vibrations was assigned at 1018 cm^{-1}. O-H stretching vibrations was appeared at 3305 cm^{-1} in nanosized CP5/P biocoagulant spectrum. This indicates the presence of O-H stretching vibrations in nanosized CP5/P biocoagulant.

In the spectrum of nanosized *Carica Papaya* seed powder, the presence of O-H bond observed at 3286 cm-1[19]. The band at 2922 cm^{-1} and 2852 cm^{-1} were assigned to the stretching of O-H bond to the methyl group (C-OH). The band showed at 1743 cm^{-1} indicate the carbonyl group of carboxylic acid or ester. The –C=O stretching of carboxylic acid with intermolecular hydrogen bond was appeared at band 1633 cm^{-1}. The band around 1236 cm^{-1} and 1053 cm^{-1} assigned to ether, ester and phenol group. By comparing the FTIR spectrum of nanosized *Carica papaya* seed powder and nanosized CP5/P biocoagulant, it was clear shows the presence of band 1633 cm^{-1} in both spectrums indicate –C=O stretching of carboxylic acid with intermolecular hydrogen bond.

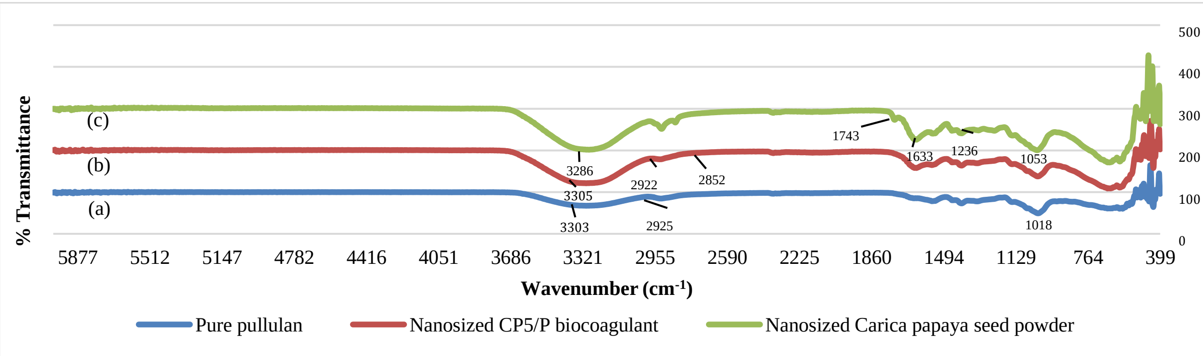

Figure 2. FTIR analysis for (a) pure pullulan (b) nanosized CP5/P biocoagulant (c) nanosized *Carica papaya* seed powder

The effectiveness of the filler modification using silane was confirmed by FTIR studies. Figure 3. shows the FTIR spectrum of pure 3-aminopropyltrimethoxysilane. The band at 1032 cm^{-1} represent the Si-O-CH_3 bonding. Band at peak 2841 cm^{-1} was indicating the presence of C-H stretching. Comparison between both biocoagulant clearly showed that Si-O-CH3 bonding was assigned at 1034 cm^{-1}. While C-H stretching can be observed at 2922 cm^{-1} and 2852 cm^{-1}.The FTIR spectrum of nanosized CP5/P treated with silane treatment, the bond O-H stretching vibrations was observed at 3305 cm^{-1} which is originated from spectrum of pure pullulan. Therefore, the band of –C=O stretching of carboxylic acid with intermolecular hydrogen bond was observed at 1633 cm^{-1} which is similar to spectrum of nanosized *Carica Papaya* seed powder in Figure 2 (c). Thus, other bands represent the silane group was overlap with those of pullulan spectrum. The bond that is related to the condensation of hydroxyl group of silane with the hydroxyl group of pullulan and those silanol self-condensation which are Si-O-C and –Si-O-Si- bridges not easily detected by FTIR since the common vibrations of these moisties around 1150 cm^{-1} and 1135 cm^{-1} are overlap by the large and intense pullulan C-O-C vibration band[10].

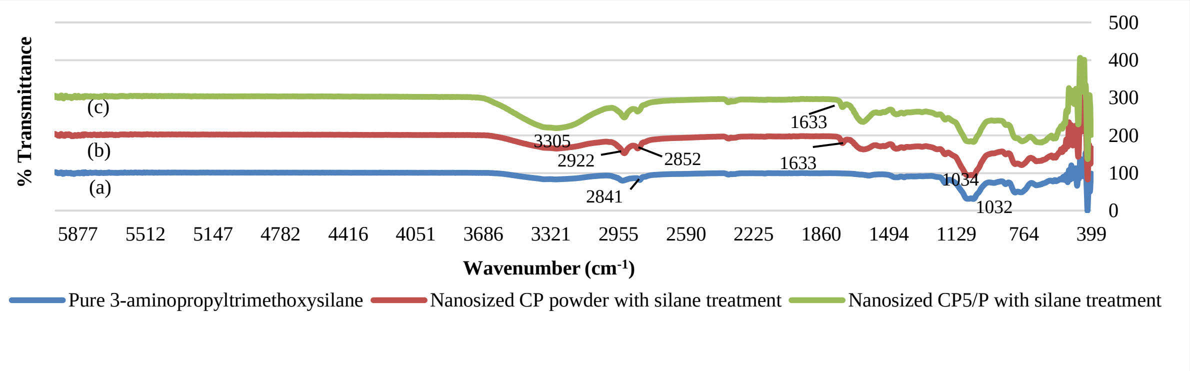

Figure 3. FTIR analysis for (a) pure 3-aminopropyltrimethoxysilane (b) nanosized *Carica papaya* seed powder with silane treatment (c) nanosized CP5/P with silane treatment.

Morphological analysis

Figure 4 shows the morphology of pure pullulan and untreated nanosized *Carica Papaya* seed modified pullulan biocoagulant. The morphological analysis was focused on the comparison between pullulan, nanosized *Carica Papaya* seed modified pullulan and silane treated nanosized *Carica Papaya* seed modified pullulan at the composition of CP5/P. As shown in Figure 4. (a) pullulan has a globous surface or smooth surface with compact surface structure. However, there is appearance of white flakes. A similar finding was obtained by Balan [16] where the white flakes are possibly due to the impurities presence in the surface of pullulan. A rough surface observed for pullulan with incorporation of CP seeds as shown in Figure 4. (b). The CP seeds were found dispersed in pullulan matrix. However, the dispersed particle was not uniformly distributed. From Figure 4. (b), the morphology indicates that the shape of CP seeds is in spherical form. The CP seeds were found tends to agglomerate as a due to hydrophilic nature. A similar finding on surface morphology of *Moringa* seed powder point out that the powder tends to form agglomerate morphology [12].

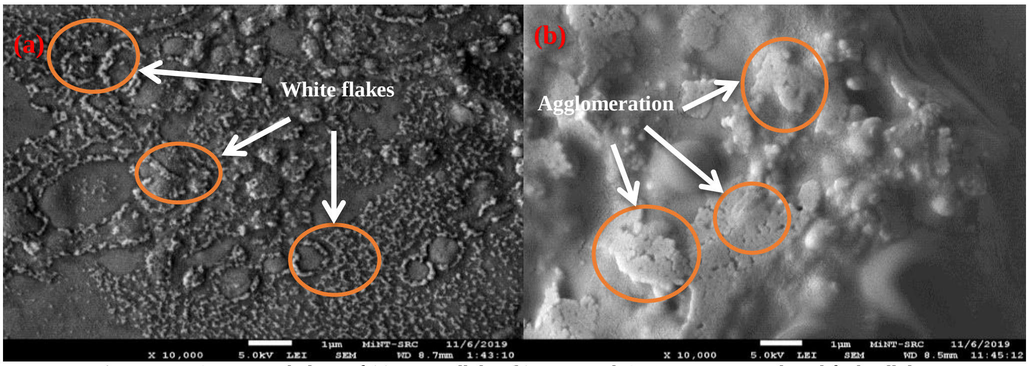

Figure 4. FESEM Morphology of (a) pure pullulan (b) nanosized *Carica Papaya* seed modified pullulan.

Figure 5 shows the morphology of the nanosized *Carica Papaya* seed powder modified pullulan with and without silane treatment. Surface roughness of nanosized *Carica Papaya* seed modified pullulan treated with silane coupling agent was increased as compared to untreated biocoagulant. The increased in surface roughness, consequently increased the surface area. Thus, provides additional sites for interlocking of the filler with matrix [16]. Penjumras [17] claimed that the silane treatment improved the surface adhesion between filler and polymer matrix. Further, it was found that the silane treatment provides well dispersion of nanosized *Carica Papaya* seed powder in the pullulan matrix phase. A similar effect observed by Penjumras [17]. It is clearly shows that more agglomeration found in the nanosized CP seed powder modified pullulan without silane treatment as compared to nanosized CP seed powder modified pullulan treated with silane coupling agent.

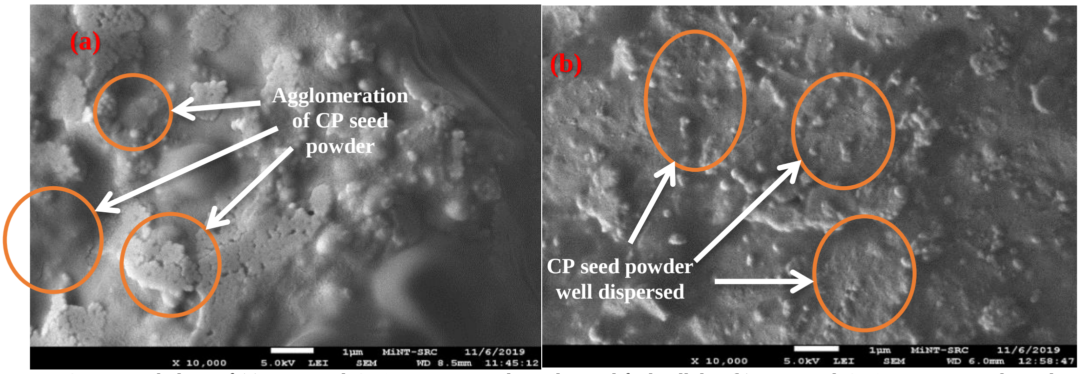

Figure 5. FESEM Morphology of (a) nanosized *Carica papaya* seed powder modified pullulan (b) nanosized *Carica Papaya* seed powder modified pullulan treated with silane coupling agent.

Wastewater Treatment analysis via jar test

The jar test analysis was summarized in Tables 4 and 5. Table 4 shows the analysis of jar test for nanosized *Carica Papaya* seed powder modified pullulan as biocoagulant followed with Table 5 for nanosized *Carica papaya* seed modified pullulan treated with silane coupling agent as biocoagulant. Each Table record the reading before and after of sewage wastewater samples.

Table 4. Nanosized *Carica Papaya* seed modified pullulan biocoagulant

Composition	Parameter								
	Turbidity			pH		DO (mg/L)		TSS (mg/L)	
	Initial (NTU)	Final (NTU)	Reduction (%)	Initial	Final	Initial	Final	Initial	Final
P100	88.17	4.44 ± 0.02	94.96	6.58	6.63	5.90	4.37	100	80
CP1/P	88.17	6.18 ± 0.04	92.99	6.58	6.66	5.90	5.94	100	60
CP3/P	88.17	5.53 ± 0.01	93.73	6.58	6.69	5.90	4.72	100	40
CP5/P	88.17	5.38 ± 0.01	93.89	6.58	6.72	5.90	4.31	100	80
CP7/P	88.17	6.84 ± 0.01	92.24	6.58	6.79	5.90	4.52	100	40
CP9/P	88.17	6.86 ± 0.02	92.22	6.58	6.78	5.90	4.45	100	40

Table 5. Nanosized *Carica papaya* seed modified pullulan treated with silane coupling agent as biocoagulant

Composition	Parameter								
	Turbidity			pH		DO (mg L^{-1})		TSS (mg L^{-1})	
	Initial (NTU)	Final (NTU)	Reduction (%)	Initial	Final	Initial	Final	Initial	Final
P100	88.17	4.63 ± 0.02	94.75	6.58	6.75	5.90	4.33	100	60
CP1/P	88.17	6.90 ± 0.01	92.17	6.58	6.73	5.90	4.20	100	60
CP3/P	88.17	5.66 ± 0.02	93.58	6.58	6.68	5.90	3.78	100	40
CP5/P	88.17	5.31 ± 0.01	93.98	6.58	6.69	5.90	4.29	100	40
CP7/P	88.17	8.34 ± 0.01	90.54	6.58	6.80	5.90	4.44	100	20
CP9/P	88.17	8.44 ± 0.05	90.42	6.58	6.86	5.90	4.44	100	60

Turbidity analysis

Figure 6 shows the turbidity reduction of untreated nanosized *Carica papaya* seed modified pullulan and nanosized *Carica papaya* seed modified pullulan treated with silane coupling agent upon wastewater treatment. The results show that each composition of biocoagulant reduced the turbidity as compared to the initial turbidity of wastewater sample.

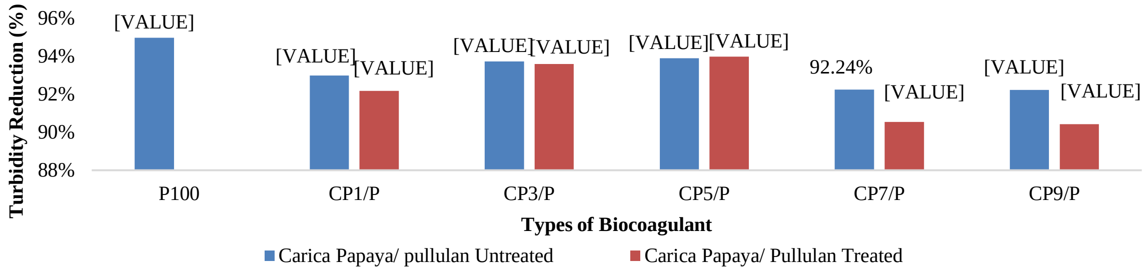

Figure 6. Turbidity reduction of untreated nanosized *Carica papaya* seed powder modified pullulan and nanosized *Carica papaya* seed modified pullulan treated with silane coupling agent upon wastewater treatment

Pullulan shows the ability to reduce turbidity up to 94.96%. This mainly due to the sticky properties of pullulan that captured all the colloids presence in the wastewater[10]. Addition of 1% CP seed decreased the turbidity reduction as compared to P100. Further reduction observed with increasing CP content from CP1/P to CP5/P. However, the turbidity reduction starts to decrease from CP7/P to CP9/9. The highest turbidity reduction of untreated nanosized *Carica Papaya* seed powder modified pullulan biocoagulant was determined at the composition of CP5/P which is 93.89%.

The turbidity reduction occurred due to the ability of protein content which acts as active compound inside the CP powder which reacted with the negative charge of colloid polluter in wastewater. Simultaneously, the sticky properties of pullulan provide a combine effect to trap the suspended compounds in wastewater. In addition, the presence of CP seed in nanosized increased the surface area exposed for the reaction and increased the solubility in wastewater. Therefore, improved the ability to reduce the turbidity of wastewater. The results are compatable with the findings reported by Hendrawati [12] who claimed that the *Moringa oleifera* nanosized (MoN) particle is more effective than *Moringa oleifera* micronsized (MoM) particle to improve the turbidity of water. MoN was capable to reduce the turbidity optimally at lower dosage compared to MoM due to the content level of the compounds. Thus, it is proved that smaller of powder, higher of active compound inside the powder [12]. A similar trend observed for nanosized *Carica Papaya* seed powder modified pullulan treated with silane coupling agent as biocoagulant where the turbidity reduction increased with increasing CP content from 1% to 5%. Therefore, the turbidity reduction starts to decrease from CP7/P to CP9/9. The highest turbidity reduction of treated biocoagulant was identified at composition CP5/P which is 93.98%. However, the percentage of turbidity reduction were slightly lower as compared to untreated biocoagulant for most of the biocoagulant composition. The uses of *Carica Papaya* seed powder as coagulant have been studied by Unnisa[8], the findings show that *Carica Papaya* seed was able to reduce turbidity up to 100%. In addition, previous study also proved that the plant-based coagulant such as orange peel able to reduce turbidity of dairy wastewater up to 97% with 0.2 g L^{-1} dosage. A similar finding was also found by Amran [7] who revealed that corn starch as coagulant effectively remove kaolin up to 98% with optimum dosage 0.5 mg L^{-1}.

Silane treatment results in no significant changes as compared to untreated nanosized *Carica Papaya* seed powder modified pullulan. This is possibly due to the hydrophobicity of this biocoagulant. A few studies proved that coagulation process efficiency is highly dependent on hydrophilic and hydrophobic properties [20]. In sewage wastewater, there is possibility to have more distribution of natural organic matter with hydrophilic characteristics. Hydrophobicity is important indicator to make sure the biocoagulant is suitable to coagulate or to trap the particle inside wastewater.

Surface modification with silane coupling agent decreased the hydrophilic character of the CP seed. Therefore, it reduced the water sensitivity of biocoagulant. This effect was clearly observed when CP/P biocoagulant applied to remove turbidity in the sewage wastewater. It is believed that the ability of CP/P biocoagulant to trap the particles that cause turbidity such as slit, humic and organic compounds was reduced due to hydrophobic surfaces. However, the unique structure of pullulan which consists of hydrophobic and hydrophilic characteristics, thus remain the ability of biocoagulant to neutralize the charge in colloidal particles and form flocs. The higher turbidity reduction for untreated nanosized CP is in agreement with study reported by Hendrawati [12]. They claimed that cationic protein produced by natural coagulant was dispersed to the wastewater thoroughly due to the interaction with negative charged particles that cause the dispersed turbidity.

pH analysis

Table 4 and 5 shows the pH of treated water for nanosized *Carica Papaya* seed modified pullulan biocoagulant and nanosized *Carica papaya* seed modified pullulan treated with silane coupling agent as biocoagulant in wastewater treatment, respectively. It can be observed that pH value of wastewater treated with P100 slightly decreased to 6.63. Similarly, the pH value of wastewater treated with nanosized *Carica Papaya* seed modified pullulan biocoagulant does not show any significant changes as compared to the initial pH of the wastewater. The pH of treated water changed to more neutral at all compositions indicating on the presence of coagulation mechanism and process.

A similar trend can be observed for pH of wastewater treated with nanosized *Carica Papaya* seed modified pullulan treated with silane coupling agent as biocoagulant. As shown in Table 5, the pH value of treated wastewater was increasing from initial pH 6.58 to the range of pH 6.68 until 6.86 where lead to more neutral. This is because polluters in water were already precipitated and the water become purer. The pH changed to neutral in line which is the clean water neutral pH [12]. Thus, the pH of treated wastewater by both biocoagulant remain stable and in the range of water quality index classification (class I) by Department of Environment (DOE) which is 6.5 until 8.5.

Dissolved Oxygen (DO) analysis

DO value of wastewater treated by nanosized *Carica Papaya* seed modified pullulan as biocoagulant was investigated. The highest DO value found at the composition of CP1/P which is 5.94 mg/L. However, the DO value starts to decrease up to 9% of CP seed. DO of nanosized *Carica Papaya* seed powder modified pullulan treated with silane coupling agent biocoagulant is decreased from composition CP1/P to CP3/P. However, the DO value starts to increase from composition CP5/P to CP9/P up to 4.44 mg L^{-1} which is the highest DO value. Overall, the value of DO in wastewater for nanosized *Carica Papaya* seed modified pullulan biocoagulant shows highest DO value in all composition, as compared to nanosized *Carica Papaya* seed powder modified pullulan treated with silane coupling agent biocoagulant. Thus, the DO value of wastewater treated by biocoagulant shows that decreasing from the initial value of wastewater. This is due to the interaction of active site of biocoagulant with oxygen atom present in water [21]. The adding of coagulant reduced the DO level due to the rise in organic substances which cause increased oxygen needs to oxidize the substances [12].

Total suspended Solid (TSS) analysis

The initial value of TSS in the wastewater sample is 100 mg L^{-1}. The TSS value of wastewater treated by nanosized *Carica Papaya* seed powder modified pullulan biocoagulant shows a decreasing trend at most of the biocoagulant composition with increasing CP loading. A slight increment observed at composition CP5/P with TSS value is 80 mg L^{-1}. However, TSS value for biocoagulant with silane treatment were gradually decreased to 20 mg L^{-1} at CP7/P. At composition of CP9/P, the TSS value increased up to 60 mg L^{-1}.

Total suspended solids (TSS) are well-defined as solids in water that can be trapped by a filter and considered as particles that are larger than 2 microns found in the water [22]. In addition, TSS specifies a variety of materials such as silt, salts, mineral acids, decaying plant or similar contaminations discharged into the water [23]. A study by Sun [24], indicates that the transparency of water is also depend on the total suspended solid value. High contents of TSS will decrease the transparency of water body. A study conducted by Pardede [25] proved that oyster mushroom biocoagulant was able to reduce the total suspended solid up to 90% in treated wastewater. In this study, TSS were able to reduce below the limit recommended by Department of Environment (DOE) in class I which below 25 mg L^{-1} at composition CP7/P.

Analysis of jar test (Coagulation Test) for Textile wastewater

Based on the result obtained for the turbidity removal for sewage wastewater, the composition with the highest turbidity removal was found at CP5/P where it chosen as biocoagulant to treat wastewater produced by textile industry. In this section, all the parameters were investigated to examine the potential of CP biocoagulant in textile industry wastewater, the results are shown in Tables 6 and 7.

Table 6. Nanosized *Carica Papaya* seed modified pullulan biocoagulant for Textile wastewater.

Composition	**Parameter**								
	Turbidity			**pH**		**DO (mg L^{-1})**		**TSS (mg L^{-1})**	
	Initial (NTU)	**Final (NTU)**	**Reduction (%)**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**
CP5/P	204	188 ± 1.00	7.84	8.12	8.27	1.87	2.37	160	100

Table 7. Nanosized *Carica Papaya* seed modified pullulan treated with silane coupling agent as biocoagulant for Textiles wastewater

Composition	**Parameter**								
	Turbidity			**pH**		**DO (mg L^{-1})**		**TSS (mg L^{-1})**	
	Initial (NTU)	**Final (NTU)**	**Reduction (%)**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**
CP5/P	204	174.33± 0.02	14.54	8.12	8.18	1.87	3.14	160	60

The turbidity value of raw textile wastewater is 204 NTU. After treated with CP5/P nanosized *Carica Papaya* seed powder modified pullulan biocoagulant and CP5/P biocoagulant with silane treatment, the turbidity removal was obtained about 7.84% and 14.54% respectively. By comparing both results, biocoagulant with silane treatment shows higher percentage of turbidity removal of textiles wastewater. This is attributed due to hydrophobic properties of biocoagulant treated with silane coupling agent, which able to bind disperse dyes effectively over large distances due to their size and structure as well as electrostatic interaction forces. In addition, the size of dye molecules or their aggregates are incomparably smaller than such inorganic particles [26]. Therefore, no significant changes observed regarding pH value and dissolved oxygen of treated textile wastewater as compared to the initial value. Thus, the textiles wastewater treated with nanosized CP5/P without silane treatment shows the changes in total suspended solid as compared to raw textiles wastewater which is about 37.5 % TSS reduction. However, the percentage reduction of total suspended solid treated nanosized CP5/P with silane treatment shows the higher reduction which is 62.5%. This indicates that the textile wastewater treated with nanosized CP5/P treat with silane treatment more effective compared to nanosized CP5/P without treatment.

CONCLUSIONS

Nanosized *Carica Papaya* seed treated silane coupling agent incorporate with pullulan were successfully prepared. The size of *Carica Papaya* seed powder was 608.9 nm which is successfully accomplished the nanosized range. It shows the better surface morphology as compared untreated CP/P. The characterization of FTIR successfully determined the chemical bonding presence in pullulan and CP seed powder when compared to the nanosized CP/P treated with silane treatment. However, the bands represent the silane group are overlap with those of pullulan spectrum. The highest turbidity reduction observed at composition of nanosized CP5/P and nanosized CP5/P with silane treatment were 93.89% and 93.98% respectively upon sewage wastewater. The effectiveness of both untreated and silane treated biocoagulant were further confirmed upon textile wastewater with turbidity reduction achieved up to 7.84% and 14.54 % respectively. In conclusion, the result obtained by using the biocoagulant to treat the wastewater had successfully achieved the objectives where its shows the potential of the biocoagulant upon wastewater treatment by decreasing the turbidity.

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Conflict of interests

No conflict.

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