Synthesis and Application of a Novel Composite Coagulant Aid from Rice Starch and Sesbania Seed Gum for Water Treatment

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This study evaluated the feasibility of a newly synthesized composite coagulant aid, SSG-S for turbidity removal in drinking water treatment. SSG-S was synthesized from rice starch and sesbania seed gum through the microwave irradiation method. The surface morphology of SSG-S was evaluated through scanning electron microscope (SEM). Compared with conventional rice starch, SSG-S provides more porous sites and longer chains for effective pollutant adsorption and bridging processes. Moreover, response surface methodology (RSM) revealed that the addition of SSG-S increased the turbidity reduction rate up to 96.3%. In addition, the novel coagulant aid helped to reduce the dosage of alum, coagulant aid, and settling period by 6.7%, 87.9%, and 6.5 minutes (1.5 times quicker), respectively.

Key words: Natural coagulant aid; response surface methodology; coagulation and flocculation; water and wastewater treatment

Received: February 2020; Accepted: September 2020

Coagulation-flocculation is the most widely used technique for water treatment since 1500 BC due to its effectiveness and simplicity [1,2]. In the current practice, the most commonly used coagulants are hydrolysing metal salts, specifically aluminium sulphate (alum) [3,4]. However, the use of inorganic chemical coagulants, i.e., aluminium sulphate (alum), has raised health concerns as the aluminium residue retained in the treated water potentially causes Alzheimer's disease [5,6]. Besides, the use of alum in water treatment may result in large amounts of aluminium-based sludges, which have been classified as scheduled waste in certain countries [7]. Therefore, natural coagulants and coagulant aids have been discovered as alternatives in replacing or minimizing the use of chemical-based coagulants as they are safe, biodegradable, and eco-friendly [8]. Starch, as one of the most abundantly available, low cost, and renewable natural polysaccharides, has gained a great deal of interest in various applications, which include water treatment [9]. Nonetheless, the application of starch in water treatment is still restricted by its medium turbidity removal efficiency. In addition, a high dosage of starch is needed to achieve good turbidity reduction, which reduces it feasibility to be used in water treatment [7,10,11]. Contrastingly, sesbania seed gum was found to be a good coagulant aid for turbidity reduction in drinking water treatment [12]. Hence, this research aims to synthesize a new starch-based composite material, SSG-S (synthezied from rice starch and sesbania seed gum) to be used in water treatment. Response surface methodology (RSM) was adopted for optimization of the newly synthesized SSG-S in coagulation-flocculation process. Conventional starch served as the control for comparison. The characterization of starch and SSG-S was performed using Scanning Electron Microscopy (SEM). In addition, the possible coagulation activities and behavior of using SSG-S as a coagulant aid in water treatment were also observed and elucidated.

MATERIALS AND METHODS

Materials

River water was used as the model sample for coagulation jar test studies. It was collected from Sultan Idris Shah (SIS II) Water Treatment Plant, located in Perak, Malaysia (4.483464, 100.913951). The pH and turbidity level of the water sample were around 6.5 and 80 NTU, respectively. Conventional rice starch and sesbania seeds were purchased from a local market and utilized for composite preparation of SSG-S and its feasibility in turbidity removal. All chemical reagents were sourced from Merck Sdn. Bhd. and of analytical grade. These included ethanol 96% (C_2H_6O) and aluminium sulfate ($Al_2(SO_4)_3$).

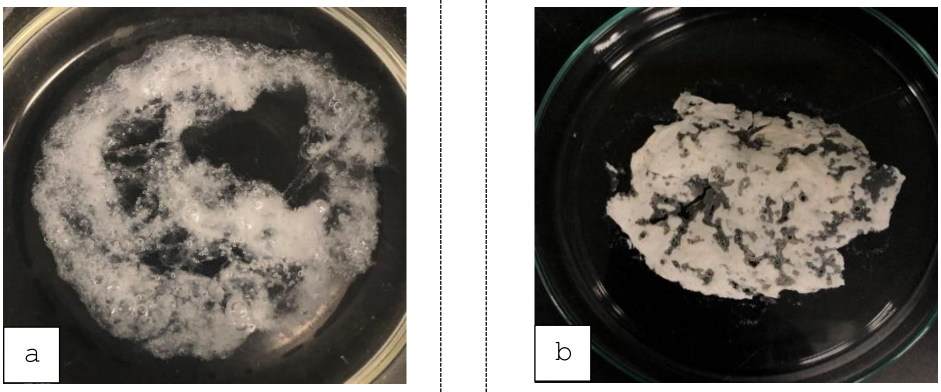

Figure 1. (a) Separation of SSG-S with the addition of ethanol, and (b) drying of SSG-S in an oven for 1 day.

Preparation of rice starch

Briefly, 300 mg of starch powder was dissolved in 40 mL of distilled water. The starch solution was mixed thoroughly and heated up to 80°C for 2 hours for starch gelatinization. The temperature of the starch solution was maintained at 80°C for subsequent use in SSG-S synthesis [3].

Synthesis of composite starch, SSG-S

15 g/L of SSG solution was prepared through dissolving 150 mg of sesbania seed gum (SSG) in 10 mL of water. Subsequently, the starch and SSG solutions were poured into a 1 L borosil beaker and mixed well. The mixture was microwaved to achieve reactive mixing using a conventional microwave oven at 700 W for 30 seconds. The mixture was then cooled down in a water bath to avoid the destruction of polysaccharide active compounds due to high temperature. The microwave irradiation and cooling cycle were repeated up to 3 minutes or the formation of a gel-like mass substance. Once the process was completed, the mixture was left to stand for 2 hours. Excess ethanol was added into the mixture to segregate water from the composite product (Figure 1(a)). Lastly, SSG-S was dried in an oven at 55°C for 1 day (Figure 1(b)) and pulverized into powder. A scanning electron microscope (SEM) equipped with energy dispersive analysis of X-ray (Perkin Elmer Spectrum) was used to observe the surface morphology of the synthesized coagulant aid, SSG-S. The dry powder of SSG-S was used as a sample for the SEM analysis.

Assay of turbidity reduction

Turbidity reduction was evaluated through jar test in accordance to the American Society for Testing and Materials (ASTM D2035) standard. A flocculator (Velp Scientifica srl-JLT6) was used in all jar test experiments. Beakers were filled with river water and put in the flocculator. Then, coagulants were added, depending on the corresponding addition mode. The jar test started with rapid mixing at a speed of 150 rpm for one minute, followed by slow mixing at 30 rpm for 20 minutes. The mixtures were then allowed to settle and samples were collected at scheduled times at around 2 cm from the bottom of the beakers using 10 mL syringes for final turbidity measurements. HACH 2100 Q turbidity meter was used to measure the turbidity of the treated water.

Response Surface Method (RSM) for evaluation and optimization studies

The traditional ‘one-factor-at-a-time’ for optimization is not only time consuming and laborious, the interactions between factors are also difficult to be determined and understood, which reduce the predictive ability. Therefore, a statistical approach, RSM is generally adopted for optimization in research and industrial sectors. In this study, Box-Behnken design (BBD) was used to optimize the factors, which involved dosage of alum, starch, and synthesized SSG-S, as well as settling period. Each factor was subjected to two levels (low and high limits). After the preliminary run of the experiment, their respective low and high limits were assigned, as shown in Table 1.

Table 1. Low and high limits of the factors

Factors	Low limit	High limit
Dosage of alum (mg/L)	9	12
Dosage of starch (mg/L)	0	20
Dosage of SSG-S (mg/L)	0	5
Settling Time (min)	1	20

RESULTS AND DISCUSSION

Surface morphologies of starch and synthesized SSG-S

Figures 2(a) and (b) show the surface morphologies of starch and SSG-S, respectively, under 5000 times magnification at 10 kV of voltage. A slightly rough surface with pores could be observed in the morphology of starch, which indicated the good flocculation properties of starch as the pores aid in the adsorption of particles and bridging process [13]. On the other hand, the synthesized SSG-S possessed rougher surface and more pores, as shown in Figure 2(b). It was expected to exert better efficiency in flocculation process as more pores were available for the binding and adsorption of suspended particles to form flocs for pollutant removal.

Effects of factors

In this experiment, 15 runs of jar test were performed using alum as coagulant, and starch and SSG-S as coagulant aids. Two ANOVA tables were generated, as shown in Tables 2 and 3, which refer to optimization studies of starch and SSG-S, respectively. In statistical approach, p-value < 0.05 refers to statistical significance of the results [14]. As shown in Table 2, p-value of the model (0.0016) indicated that the model was significant and reliable. Furthermore, p-value of all the individual factors, which were dosage of alum (<0.0001), dosage of starch (0.0451), and settling time (0.0236) confirmed the significant factors in turbidity reduction.

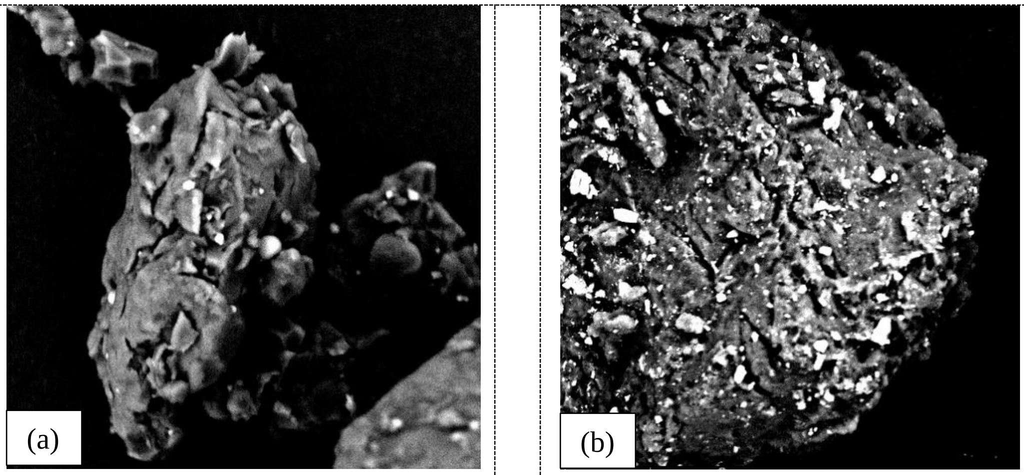

Figure 2. Surface morphologies of (a) starch and (b) SSG-S under 5000 times magnification.

Table 2. ANOVA table for factors optimization using starch as coagulant aid in water treatment

Source	Sum of Squares	Mean Square	F Value	p-value
Model	5490.20	610.02	37.54	0.0016*
A-Dosage of Alum (x_1)	4906.23	4906.23	301.90	< 0.0001*
B-Dosage of Starch (x_2)	134.57	134.57	8.28	0.0451*
C-Settling Time (x_3)	205.66	205.66	12.65	0.0236*
AB (x_1x_2)	4.01	4.01	0.25	0.6454
AC (x_1x_3)	52.13	52.13	3.21	0.1478
BC (x_2x_3)	72.06	72.06	4.43	0.1030
A^2 (x_1^2)	7.20	7.20	0.44	0.5421
B^2 (x_2^2)	30.30	30.30	1.86	0.2439
C^2 (x_3^2)	73.49	73.49	4.52	0.1006
Lack of Fit	63.19	21.06	11.58	0.2120

* Significant
~ R-Squared: 0.988

Table 3. ANOVA table for factors optimization using SSG-S as coagulant aid in water treatment

Source	Sum of Squares	Mean Square	F Value	p-value
Model	3791.55	421.28	50.27	0.0009*
A-Dosage of Alum (x_1)	2804.16	2804.16	334.62	< 0.0001*
B-Dosage of SSG-S (x_2)	88.05	88.05	10.51	0.0316*
C-Settling Time (x_3)	124.49	124.49	14.85	0.0182*
AB (x_1x_2)	13.09	13.09	1.56	0.2795
AC (x_1x_3)	103.57	103.57	12.36	0.0245*
BC (x_2x_3)	3.08	3.08	0.37	0.5771
A^2 (x_1^2)	626.14	626.14	74.72	0.0010
B^2 (x_2^2)	3.49	3.49	0.42	0.5541
C^2 (x_3^2)	75.00	75.00	8.95	0.0009
Lack of Fit	31.81	10.60	6.19	0.2853

* Significant
~ R-Squared: 0.991

However, the interactions between the factors were not statistically significant (p-value> 0.05). R^2 of the model at 0.988 proved the reliability of the model as 98.9% of total variance is well explained. Meanwhile, the model shown in Table 3 for synthesized SSG-S optimization was also significant at p-value < 0.001. Similarly, all the individual factors and the interaction between alum and settling time were also statistically significant (p-value < 0.05). By comparison between optimization of starch and SSG-S, p-value of SSG-S dosage at 0.0316 was much lower than starch dosage at 0.0451. It could be hypothesized that newly synthesized SSG-S encompassed higher flocculating ability with lower quantity needed in turbidity reduction to meet the legislative requirement of water quality. The R^2 obtained for the model (0.991) showed the close approximity of the results.

Figures 3 and 4 illustrate the 3D response surfaces of the designed factors when starch and SSG-S were used as the coagulant aids for water treatment, respectively. The interactions between dosage of alum with starch and alum with SSG-S are shown in Figures 3(a) and 4(a), respectively, where high turbidity reduction could be achieved when the dosage of alum was in the range of 11 – 12 mg/L, accompanied by the dosage of starch in the range of 12 - 18 mg/L. When SSG-S was used as the coagulant aid, more than 95% turbidity removal could be attained with the dosage of alum and SSG-S around 10.5 - 12 mg/L and 1 - 5 mg/L, respectively. This could be attributed to the role of alum in destabilization of negatively charged particles in the water through charge neutralization. After the particles lost their stability, starch as the coagulant helped to link and bind the particles using its long polymer chains to form larger flocs, in which the mechanism is known as bridging mechanism. As SSG-S carries more porous surface characteristics, more binding spaces are available for high turbidity removal with only small dosages. For the interaction between dosage of alum and settling time (Figures 3(b) and 4(b)), increase of alum dosage reduced the settling time of flocs. When a large amount of alum was added into the water, more particles would be destabilized, which led to the formation of a large amount of aluminum hydroxide precipitates to adsorb the suspended particles, and consequently flocs settled faster. The interactions between dosage of starch and settling period and SSG-S dosage and settling time are illustrated in Figures 3(c) and 4(c), respectively. To achieve high turbidity reduction, the dosage of starch is inversely proportional to the settling time until it reaches an optimum condition where prolonged settling time will have only little effect on turbidity reduction. Appropriate dosages of starch and SSG-S could effectively link and bind anionic particles via stretching of active compound segments presented in starch to form stronger and larger flocs, which minimizes the settling time. However, overdose of starch and SSG-S may trigger steric stabilization attributed to the increase of polymer binding and adsorption beyond the optimum control [5]. Consequently, the turbidity removal rate is reduced.

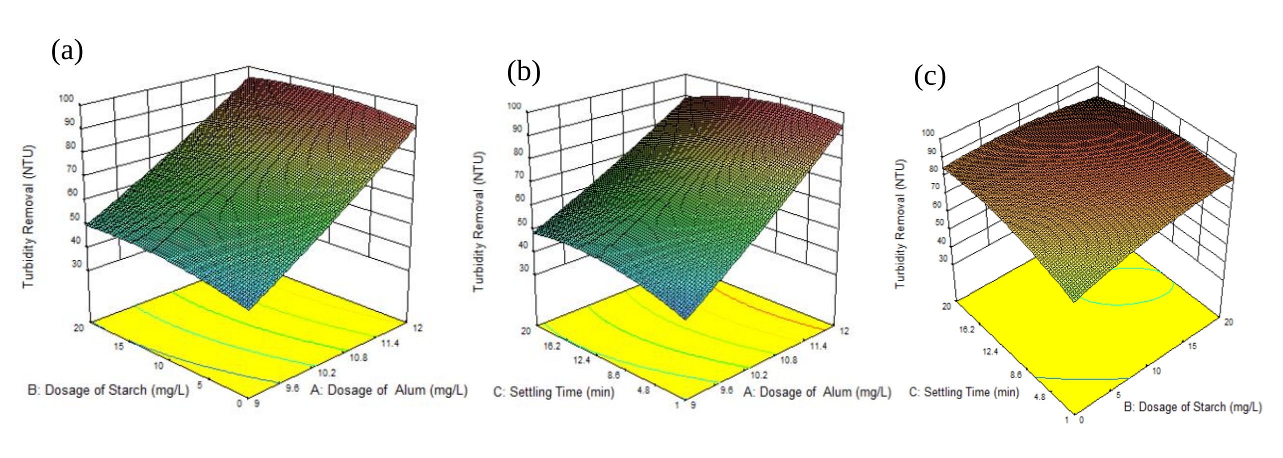

Figure 3. 3D response surface of the designed factors (starch as coagulant aid).

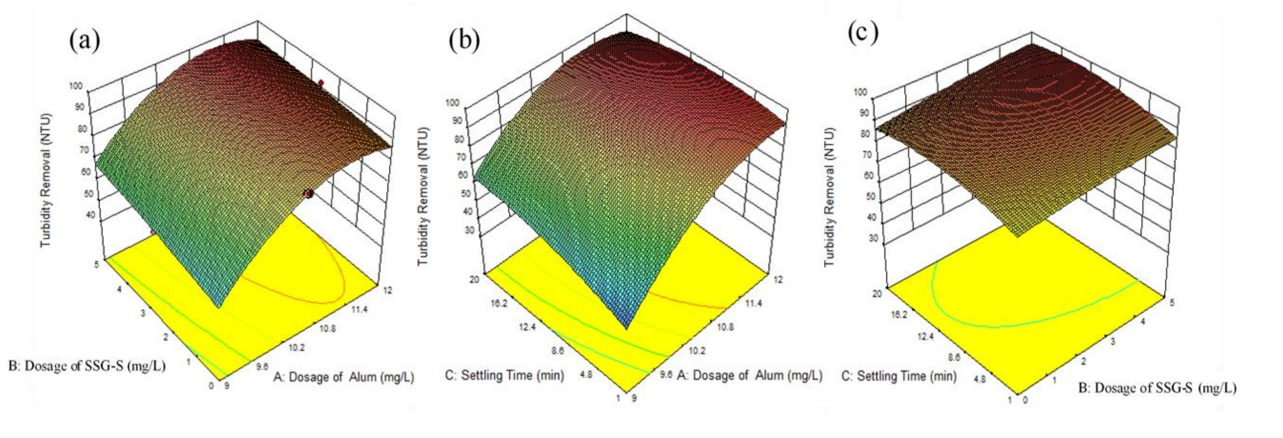

Figure 4. 3D response surface of the designed factors (SSG-S as coagulant aid).

Optimization of starch and SSG-S as coagulant aids

The optimum conditions for each designed factor were predicted by the model as shown in Table 4. The results showed that 94% of turbidity reduction could be achieved with 12 mg/L of alum, 16.5 mg/L of starch, and 16.5 minutes of settling time. In contrast, a slightly higher turbidity reduction (96.3%) could be attained with 11.2 mg/L of alum, 2 mg/L of SSG-S, and 10 minutes of settling time. By using SSG-S as the coagulant aid, it reduced up to 6.7% of dosage of alum, 87.9% of coagulant aid, and 39.4% of settling time, while achieving 2.4% higher turbidity reduction, as compared to starch. These results illustrated that synthesized SSG-S accommodated higher efficiency in turbidity removal with lower dosage as compared with conventional starch. This was not only accredited by its higher porous surfaces, but also higher molecular weight through reactive grafting of starch and SSG. When a mixture of starch and SSG is irradiated using microwaves, small polar molecules, i.e. water, will generate heat due to the rotation and collision of the molecules. Apart from water molecules, larger molecules such as starch or SSG are irradiated by microwaves as well. However, the entire molecule is not possible to rotate. Therefore, the polar groups present in starch, i.e. hydroxyl group, and SSG will absorb the microwaves and consequently severing of hydroxyl bonds will occur, which creates free radical sites [15,16]. Evidently, the free radical sites formed will recombine together through a few steps, which include initiation, propagation, and termination steps to produce SSG-S with high molecular weights and longer polymer chains [17]. The proposed structure of SSG-S is shown in Figure 5. High molecular weights and longer polymer chains of SSG-S enable it to adsorb and bind more destabilized particles to form larger flocs in water through bridging mechanism, and hence the dosage of SSG-S as coagulant aid and settling time can be greatly reduced.

Table 4. Optimum conditions of designed factors by using starch and SSG-S as coagulant aids

Source	Coagulant Aids		Differences (%)
	Starch	SSG-S	
Dosage of Alum (mg/L)	12.0	11.2	6.7
Dosage of Coagulant Aid (mg/L)	16.5	2.0	87.9
Settling Time (minutes)	16.5	10	39.4
Turbidity Reduction (%)	94.0	96.3	2.4

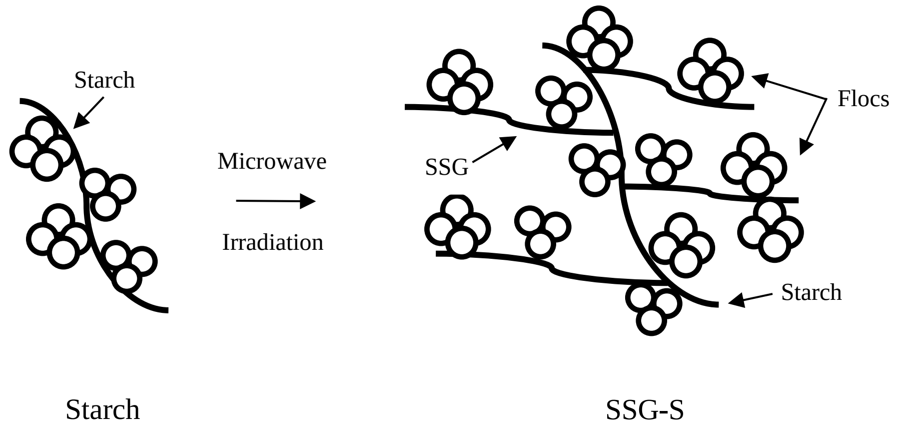

Figure 5. Proposed structure of SSG-S after the microwave irradiation.

Eq. (1) shows the second-order regression model of turbidity reduction in terms of coded variable when starch was used as the coagulant aid in the water treatment. In contrast, Eq.(2) shows the second-order regression model when SSG-S was used as the coagulant aid. These equations were used to predict the turbidity reduction for the given levels of factors. The positive sign of the coefficient represents the positive effect of the factor on turbidity reduction and vice versa [18].

$$\text{Turbidity reduction} = 69.99 + 24.76x_1 + 4.10x_2 + 5.07x_3 - 1.00x_1x_2 - 3.61x_1x_3 - 4.24x_2x_3 + 1.50{x_1}^2 - 3.08{x_2}^2 - 4.79{x_3}^2 \quad (1)$$

$$\text{Turbidity reduction} = 91.37 + 18.72x_1 - 3.32x_2 + 3.94x_3 - 1.81x_1x_2 - 5.09x_1x_3 + 0.88x_2x_3 - 13.99{x_1}^2 - 1.04{x_2}^2 - 4.84{x_3}^2 \quad (2)$$

Table 5. Validation test

Dosage of Alum (mg/L)	Dosage of Coagulant Aid (mg/L)	Settling Time (mins)	Turbidity Reduction (%)		Differences (%)
			Predicted	Actual	
Starch as coagulant aid					
12.0	16.5	16.5	94.0	92.4	1.6
10.5	10.0	10.5	70.0	71.3	1.3
9.0	3.54	10.0	49.0	51.9	2.9
SSG-S as coagulant aid					
11.2	2.0	10.0	96.3	97.1	0.8
9.3	1.5	20.0	68.0	70.5	2.5
9.0	0	6.0	47.2	43.9	3.3

Validation

Validation test is significant to prove the accuracy and reliability of the developed regression models. A total of six sets of the experimental runs were randomly selected for starch and SSG-S. The outcomes of the chosen combinations of alum dosage, starch and SSG-S dosage, and settling time are presented in Table 5. The differences of the predicted and actual turbidity reduction for all six runs were less than 5%. Therefore, it could be concluded that the predicted models for optimization were accurate and in good consistency with the experimental results.

CONCLUSION

A novel highly-efficient coagulant aid, SSG-S was synthesized through microwave irradiation method. SEM analysis confirmed the success of synthesizing SSG-S with higher porous sites for effective particle adsorption and bridging. Response surface methodology (RSM), specifically BBD, was used to evaluate and optimize the factors for water treatment. The optimum operating conditions of SSG-S as a coagulant aid were with 11.2 mg/L of alum, 2.0 mg/L of SSG-S, and 10 minutes of settling time to achieve up to 96.3% of turbidity reduction. Compared with water treatment using conventional starch, SSG-S could reduce around 6.7% of dosage of alum, 87.9% of coagulant aid, and 6.5 minutes (1.5 times) of settling time. These results revealed the potential of using SSG-S in water treatment for effective turbidity reduction. Further characterization and analyses of SSG-S are necessary for better elucidation of novel mechanisms of coagulation-flocculation process in water treatment.

ACKNOWLEDGEMENTS

The authors would like to thank PETRONAS for funding this research under YUTP grant (0153AA-E34). Furthermore, the authors would also like to express their gratitude to Mdm. Norhayama Bt Ramli of the Environmental Research Laboratory for her various technical support.

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