CHEMICAL ENGINEERING TRANSACTIONS
VOL. 45, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216
DOI:10.3303/CET1545247

Natural, Biodegradable and Non-Toxic Coagulant from g. *Hylocereus* Foliage: Optimisation on Coagulant Preparation

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This g. Hylocereus foliage has high potential to be an environmental friendly, natural based coagulant to substituting the conventional chemical metal formulated coagulant. In this study, we focused on the optimization of the condition for the preparation of coagulant through response surface methodology. A preliminary experiment was performed to screen-out insignificant parameters. The effect of drying temperature, extraction temperature and extraction duration towards the turbidity removal and viscosity of g. Hylocereus extract (g.H.E.) were studied. The model developed for turbidity removal and viscosity were the quadratic and linear model. Optimization done using numerical method found the optimum condition of drying temperature of 46.51 °C, extraction temperature of 100 °C and extraction duration of 20 min. At these condition, the turbidity removal and viscosity were 97.2174 % and 30.3411 mPa•s with desirability of 0.927.

1. Introduction

Aluminium sulphate (Alum) and polyaluminium chloride (PAC) are the conventional chemical metal formulated coagulant used in the water treatment facilities. These chemical coagulants are commonly used in water treatment facilities because, they are cheap, easy to be stored and prepared, and they are very effective in removing suspended solid. For so many decades, the treatment facilities use these chemical for treating water and knowing little of the side effect until recently (Pearse, 2003). After the treatment, Traces amount of aluminium ions could be found and will affect our health directly through drinking water and indirectly through our food sources such as fishes. There are many researches did study the effect of aluminium found in our drinking water towards our health and most of them concluded that, aluminium could cause many neurological diseases such as Alzheimer's Disease (Flaten, 2001).
These issue motivated many researches to research on a natural based coagulant which is more environmental friendly, and safer as a substitution of the conventional chemical coagulant. Natural coagulant is a not a modern invention, in fact, they exist since in ancient time and also in the rural area (Hameed and Ali, 2014). The main problems of faced would be lack of understanding of the working mechanism, and active component. The most popular natural coagulant studied would be the *Moringa Oleifera* seed or commonly called Drumstick Tree seed (Francis and Amos, 2009). The active component was reported to be a water cationic protein (Ahmad et al., 2006). No doubt that, *Moringa Oleifera* seed is very effective in removing suspended solid, however, the seed itself is also a food source for some natives and there is no large scale plantation available to support the uses of *Moringa Oleifera* seed as a coagulant.
Besides *Moringa Oleifera*, *Opuntia* spp., a pear cactus was reported to be effective in removing suspended solid. Miller et al. (2008) claimed that, the working mechanism of the *Opuntia* spp. is physical bridging mechanism instead of neutralisation of charge. The active component suspected to be starch or polysaccharides found in the mucilage cell (Miller et al., 2008). Similarly, the genus *Hylocereus* is a night blooming cactus which belonging to the family of *Cactaceae*, it is usually called pitaya or dragon fruit. The fleshy succulent foliage is the main part of the plant, which is green in colour and usually appeared in 3 pointed star shape lobbed with its ridge and equipped with small thorns. The foliage can grow up to 2 m long.

Please cite this article as: Jun L.E.F., Ahmad A.L., 2015, Natural, biodegradable and non-toxic coagulant from g. hylocereus foliage: optimisation on coagulant preparation, Chemical Engineering Transactions, 45, 1477-1482 DOI:10.3303/CET1545247

From a preliminary study, it was found that g. *Hylocereus* extract (g.H.E.) has a similar result from the *Opuntia* spp. The purpose of this paper is to determine the optimum condition for the preparation of g.H.E. through response surface methodology (RSM) with the aids of Design-expert software (Version 6.0.6 by Stat-Ease. INC, MN, USA). There are 4 independent variables that needed to be optimised in the process, which are the drying temperature, extraction medium, extraction temperature and extraction duration. RSM is chosen due to its effectiveness in optimizing a process when the independent variables are having a combine effect (Koocheki et al., 2009). The software requires series of experiment with which different combination of independent variables were applied. From the result of experiment, optimum condition will be determined by the software after gone through analysis of variance (ANOVA).

2. Material and Methodology

2.1 Materials

The g. *Hylocereus* foliage were collected from the residential area in Ipoh, Malaysia. All chemicals used in this studies were analytical graded except those which specifically mentioned.

2.2 Preparation of Coagulant

The thorns on the foliage were removed with scissor. Then, the foliage were washed with distilled water to remove impurities on the foliage. After that, the foliage were sliced into smaller pieces around 1-2 cm in width and length. The pieces were dried in an oven at designed temperature for 24 h. The dried pieces were ground using a commercial Electrofast blender (model EFO13QBL014O). The ground foliage was kept in refrigerator. The ground foliage was dissolved into distilled water to prepare 1 % w/v coagulant. The mixture were stirred using a hot plate magnetic stirrer at designed temperature and duration. The extract was filtered out with a cheese cloth to separate the residue. The filtrate is ready to be used as g. *Hylocereus* Extract (g.H.E) coagulant. The extract was kept in the refrigerator.

2.3 Preparation of Turbid Water

10 g of Kaolin powder was dissolved into 1 L of tap water. The suspension was stirred for 60 min at room condition with a magnetic stirrer. Then, the suspension was left on standing for 24 h to allow complete hydration of the kaolin particles. The suspension was kept as a stockpile suspension and stored in dry and cool place.

2.4 Viscosity Measurement

The viscosity of the g.H.E prepared was measured using Brookfield Viscometer (model DV2T with DV2TLV-01 spindle). The measuring model was set as multipoint configuration with duration of 1 min and 30 s to obtain average reading. The speed of rotation was adjusted until the accuracy is less than around 1 % and the % torque is within the range of 10 – 100 %.

2.5 Turbidity Measurement

Turbidity was measured with HACH Portable Turbidimeter (Model 2100P). The unit for the turbidity measured is in Nephelometric Turbidity Unit (NTU). The initial turbidity of the turbid water before jar test was measured and the turbidity after treatment was measured again. The turbidity removal was calculated out with Eq(1).

$$\text{Turbidity Removal (\%)} = (1 - Tbdt_{final} / Tbdt_{initial}) \times 100\ \% \quad (1)$$

where Tbdt is the turbidity measured

2.6 Jar Test Experiment

The jar test experiment was conducted by using commercial jar test apparatus. The Kaolin suspension from the stockpile was adjusted to 200 NTU and pH 7. Then, 500 mL of suspension prepared was poured into 4 different 500 mL beakers. The suspensions were then placed in the jar test apparatus. Different dosage of g.H.E. range from 5 – 30 mg/L were added into the suspensions. Initially, the suspension underwent rapid mixing with speed of 110 rpm for 1 min, then followed by slow mixing 20 rpm for 30 min. After that, the suspensions were allowed to settle for 30 min. The supernatant was collected around at 2 cm below the water surface, then the turbidity of the supernatant was measured. The dosage of g.H.E. for 500 mL of turbid water was calculated out according to Eq(2)

$$\text{Dosage (mg/L)} = \text{Volume of g.H.E added to 500 mL turbid water (mL)} \times 20 \quad (2)$$

2.7 Design of Experiment and Statistic Analysis

Response surface methodology (RSM) was implemented to study the effect of independent variables (i.e. drying temperature, x_1, extraction temperature, x_2 and extraction duration, x_3) towards the turbidity removal (%), and viscosity (mPa•s). The independent variables were the result from the preliminary experiment. Preliminary experiment helps to determine the dominant effect and eliminating the insignificant variable. (Kumar et al., 2009). Salt and solvent as the medium of extraction were tested to be having negative impact on the performance. Hence, they were eliminated from the experiment. A central composition design (CCD) with face-centred (i.e. alpha value = 1) was implemented for designing the experiment data.

The RSM was applied to the experiment data with a commercial statistical package, Design-Expert version 6.06 by Stat-Ease Inc. The experiment was conducted with full 20 sets of experiments with 14 not centre points and 6 centre points to calculate the repeatability of RSM (Koocheki et al., 2009). The quadratic model for predicting the optimum condition during preparation could be expressed as shown in the Eq(3) which related the response to the coded variable.

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \varepsilon \quad (3)$$

The coefficient of the quadratic polynomial were represented by β, where β_0 is the constant term, β_1, β_2 and β_3 are the linear effect's coefficient, β_{11}, $\beta 2_2$ and $\beta 3_3$ are the quadratic effect's coefficient, β_{12}, β_{13} and β_{23} are the interaction effect's coefficient while ε is the random error.

The analysis of variance (ANOVA) was done after the experiment were done. The significant terms in the model generated were determined and those which were insignificant were unselected. The significant term was evaluated by its Prob>F value which is advisable to has a value of less than 0.0500. (Ghafari et al., 2009). The model was qualified through its R^2 value and Adjusted-R^2 value.

Numerical optimization method was implemented to determine the optimum value of variable. The goal for all the independent variables were set as 'in the range', while the goal for the responses were either 'maximum' or 'minimum'.

3. Results and Discussion

3.1 Model Fitting

Initially, quadratic Eq(3) was fit to each of the responses (i.e. turbidity removal, corresponding dosage, and viscosity). After the result from sequence model sum of square was analysed, the most significant model was selected. A model with the highest order and the lowest Prob>F or p-value indicates the model is significant. Cubic model was found to be aliased. Aliased model indicates that, the model is not suitable for further study as mentioned by an author (Kumar et al., 2009). This is because there is insufficient experimental data to independently estimate all the terms for that model. The fit summary for each of the response is shown in the Table 1. From the fit summary, the model suggested for turbidity removal, and viscosity are quadratic and linear.

ANOVA is a statistical method to test the significant terms of the model suggested. It provided the coefficient of terms in the polynomial and theirs corresponding *p*-value. In addition, the lack of fit was calculated together with the value R^2, adjusted-R^2 and coefficient of variance, CV were calculated to examine the model adequacy. Similarly, the *p*-value indicates that how significant the term of the polynomial is. The terms with *p*-value greater than 0.0500 were eliminated. The significant term were tabulated in the Table 2. Lack of fit indicates the quality of model fits. When a model with a significant lack of fit (i.e. *p*-value < 0.0500), it means that the model unable to adequately relates the independent variables and the response variables. The model generated for both turbidity removal and viscosity , the *p*-values are greater than 0.0500, which these model have no significant lack of fit.

Table 1: Sequential model sum of square

Source	DF	Turbidity Removal		Viscosity	
		Sum of Square	*p*-value	Sum of Square	*p*-value
Mean	1	142,000		10,364.9	
Linear	3	1,705.46	< 0.0001	368.1	< 0.0001
Interaction	3	167.27	0.2352	1.56	0.7432
Quadratic	3	425.87	< 0.0001	0.35	0.9727
Cubic	4	17.72	0.0649	13.77	0.0081
Residue	6	6.66		2.07	
Total	20	144,000		10,750.76	

Table 2: ANOVA for the response variables (actual values)

Source	Turbidity Removal				Viscosity			
	Coefficient	DF	Sum of Square	*p*-value	Coefficient	DF	Sum of Square	*p*-value
Model	2,286.67	6	2,286.67	< 0.0001	31.80462	3	368.1	< 0.0001
Linear								
β_1	2.53296	1	1,135.66	< 0.0001	-0.32253	1	234.06	< 0.0001
β_2	-0.029696	1	536.32	< 0.0001	0.095457	1	111.62	< 0.0001
β_3	0.24399	1	33.49	0.0042	0.1996	1	22.41	0.0004
Quadratic								
β_{11}	-0.034487	1	192.67	< 0.0001	-	-	-	-
β_{22}	-0.00174	1	14.59	0.0397	-	-	-	-
β_{33}	-	-	-	-	-	-	-	-
Interaction								
β_{12}	0.00846	1	157.96	< 0.0001	-	-	-	-
β_{13}	-	-	-	-	-	-	-	-
β_{23}	-	-	-	-	-	-	-	-
Residual	-	13	36.32	-	-	16	17.76	-
Lack of Fit	-	8	29.66	0.1373	-	11	15.7	0.0909
Pure Error	-	5	6.66	-	-	5	2.06	-
Total	-	19	2,322.99	-	-	19	385.86	-
R^2	0.9844	-	-	-	0.954	-	-	-
Adj-R^2	0.9772	-	-	-	0.9453	-	-	-
CV	1.98	-	-	-	4.63	-	-	-

The coefficient of determination R^2 indicates the goodness of the model. The higher the value of R^2, the more relevant dependant variables in the model have to describe of the behaviour variation (Mendenhall et al., 2012). However, the addition of terms to the model will always increase the value of R^2, regardless the additional term is whether statistically significant or not. So, a large value of R^2 is insufficient to evaluate the adequacy of the model. Hence, adjusted-R^2 of more than 90 % is more appropriate to be evaluate the model's adequacy (Koocheki et al., 2009). Besides, the adjusted-R^2 should also advocates a high correlation between the observed and the predicted values (Kumar et al., 2009). The R^2 and adjusted-R^2 for both our model are greater than 94 % which means our model is adequate and suitable to explain the behaviour.

Furthermore, the coefficient of variation (CV) as the ratio of the standard error of estimate to the mean value of the observed response defines reproducibility of the model (Ghafari et al., 2009). The higher the CV value the higher the variation in the mean value which does not satisfactorily develop an adequate response model (Koocheki et al., 2009). The CV value should not greater than 10 % (Dahmoune et al., 2014). Our results shows the coefficient of variance were 1.98 and 4.63.

Figure 1 shows each of the experimental value compared to that of predicted by the regression model. The results shows that the models were able to identify the operating condition during the preparation of g.H.E.

3.2 Turbidity Removal

From the model of turbidity removal, all linear effects were significant. Quadratic and interaction effect of drying temperature and extraction temperature were significant as shown in the Table 2. Those terms which were insignificant were discarded. According to the value of sum of square, the independent variable could be arranged in the order of drying temperature > extraction temperature > extraction duration. The results also showed that the variable with the largest effect would be linear and followed by quadratic and interaction. The response surface based on the model terms listed in Table 2 was generated and shown in Figure 2. The surface was generated by varying drying temperature and extraction temperature while the extraction duration was kept at constant (20 min). The maximum predicted value would be the located at the region bounded by the smallest ellipse in the contour or the highest points on the 3D surface. At high drying temperature, the turbidity removal decreased. Drying at high temperature may cause the starch/polysaccharide to undergo mechanical damage as explain (Malumba et al., 2009). At low drying temperature, the turbidity removal slight decreased, this is due to the moisture content in the g. Hylocereus foliage was relatively higher than the optimum. This decreased the concentration of the active component in g.H.E. However, the highest the extraction temperature, the highest the turbidity removal, same things go to the extraction duration. At high temperature, the solubility of the active component suspected to be increased and the longer the extraction duration, the greater the amount of the active component extracted out which is similar to the explanation by this author (Koocheki et al., 2009)

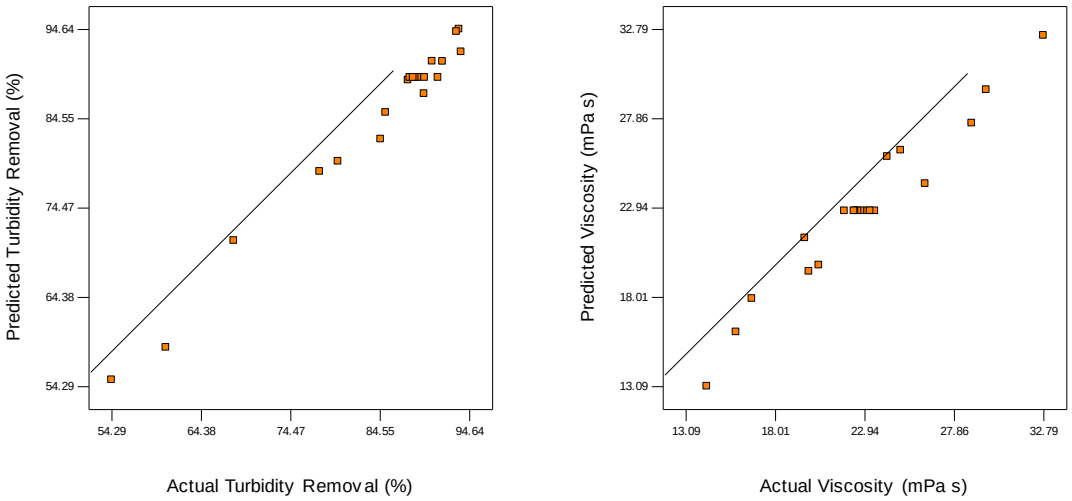

Figure 1: Comparison of actual and predicted value of turbidity removal (left), and viscosity of g.H.E. (right)

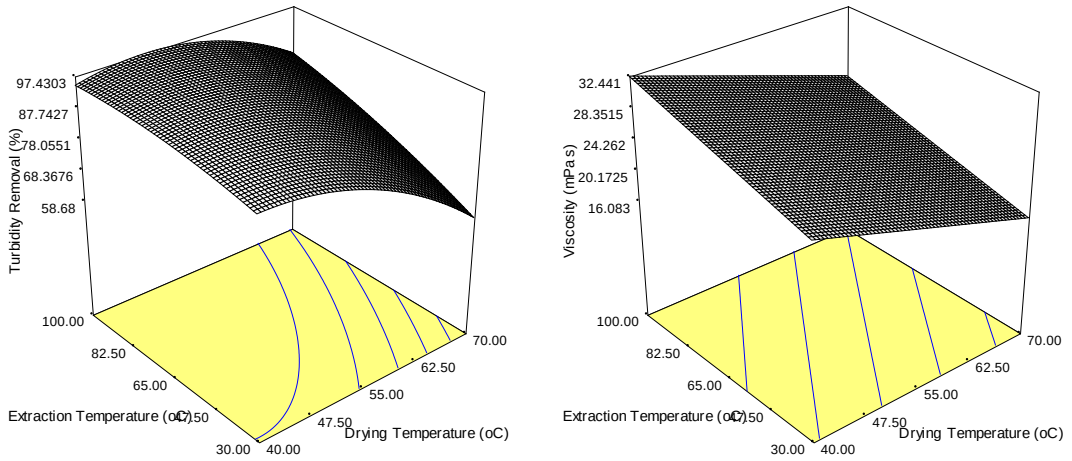

Figure 2: The response surface of effect of drying and extraction temperature at extraction duration = 20 min of turbidity removal (left), and viscosity of g.H.E. (right)

3.3 Viscosity

It should be noted that, the highest the viscosity, the highest the turbidity removal. Only linear effect were significant to the response. Similarly, the drying temperature and extracting temperature were the dominant effect. The significant order of the independent variable were the same as that disused in section 3.2. A surface response with the same condition as the previous one was plotted in Figure 2. Similarly, the viscosity was low at high drying temperature. As mention earlier, high drying temperature did mechanical damage on the active component (Güler et al., 2002). The author claimed that the viscosity was decreased as temperature-time increased, due to irreversible change in the chemical structure of the starch (Koocheki et al., 2009). The observation was different from our results. The reason of the difference was that, our extraction time was much shorter than that studied by the author, besides, Singthong et al. (2009) also concluded that, the higher the extraction temperature and duration were results in higher viscosity.

3.4 Optimization

The optimum condition for g.H.E. preparation was determined to maximise the turbidity removal and viscosity. The optimum condition and the respective response were tabulated in Table 3. The highest response provided for turbidity removal was 97.2174 % and the highest viscosity was 30.3411 mPa•s. The highest viscosity obtained was slightly less than that of maximum (32.441 mPa•s) modelled, but it is still in acceptable range.

Table 3: Optimum condition for g.H.E. preparation. (Numerical)

Variable	Goal	Lower	Upper	Optimized	Reliability
Drying Temperature (^{o}C)	Is in range	40	70	46.51	0.927
Extraction Temperature (^{o}C)	Is in range	30	100	100	
Extraction Duration (minute)	Is in range	5	20	20	
Turbidity Removal (%)	Maximum			97.2174	
Viscosity (mPa•s)	Maximum			30.3411	

4. Conclusion

The results from the RSM showed that the effects of independent variables namely drying temperature, extraction temperature and extraction duration were statistically significant on our g.H.E. preparation. Quadratic models were developed for turbidity removal while linear model for viscosity. Drying temperature had the most significant effect. In overall, the higher the drying temperature, the lower the turbidity removal and viscosity. While the increasing in the extraction temperature, the turbidity removal and viscosity increased. Furthermore, the longer the extraction duration, the higher the turbidity removal and viscosity. In order to obtain the maximum turbidity removal and viscosity, the optimum drying temperature, extraction temperature and extraction duration were 46.51 °C, 100 °C and 20 min. This research could benefits the further study of g. *Hylocereus* foliage coagulant and the future development.

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