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Development of Natural Coagulant from Matured Petail Belalang Peel

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Abstract: This study investigates about the development of natural coagulant by extraction of coagulant from matured Petai Belalang peel due to its eco-friendly characteristic. Coagulant commonly used in wastewater treatment as alternative method in the treatment of wastewater due to cost effective. Chitin as natural coagulating agent in the matured Petai Belalang peel has been extracted using HCl solution in three different concentrations of 1.0, 2.0 and 3.0 M. Two different analysis techniques have been employed to characterize the obtained chitin. Characterization of obtained chitin for the functional groups of chitin has been studied by Fourier Transform Infrared Spectroscopy (FTIR) and the thermal properties were analyzed by Differential Scanning Calorimetry (DSC) for both extracted chitin and dried peel. The IR spectra of extracted chitin in 1.0 M solution showed the most similar corresponding band with the commercial chitin and displayed of α-chitin formation. The endothermic peaks and exothermic peaks for both extracted chitin and dried peel were studied on correspond towards loss of water and decomposition of polymer, respectively by DSC curve. From the observations, the curves showed the first peaks is corresponding to the loss of water around 70° upto 90°C and second peaks due to relaxation of endotherm around 120°-150°C. The dried peel in 1.0M solution, exothermic peaks showed around 300°C is corresponding to the decomposition of polymer in chitin. However, due to aging peel as raw material the chitin polymer may have degraded under the sun and reduced the chitin polymer content in the peel, therefore the exothermic peaks are not present in high concentration solution. Last but not least, it can be concluded that 1.0 M solution is the most suitable for chitin extraction in development of natural coagulant from matured Petai Belalang peel.

Key words: Coagulant, chitin, FTIR, DSC, matured Petai, wastewater

INTRODUCTION

The most vital element among the natural sources is water. Natural organic matter is an important issue for water industries because it can causes the water to be colored, high chemical demand, lowers disinfectant residual and as a substrate for microbial growth in distribution system. The treatment of water mostly relies on coagulation, sedimentation, filtration and disinfection process. Due to the lack of proper water treatment systems in rural or undeveloped communities, the best option is to use simple and relatively cost effective point of use technologies such as coagulant. According to Mengistie *et al.* (2008) numbers of treatment technologies have been used for wastewater treatment such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation and electro-remediation method. However, due to its disadvantages for unable in removing heavy metal at low concentration and relatively high cost method. Therefore, a simple and effective low cost treatment technique such as coagulation is desirable. Various treatment method have been employed include chemical reduction and precipitation, ion exchange, liquid extraction, reverse osmosis and membrane filtration (Babu and Gupta, 2008). Adsorption and coagulation methods are great method for removal of water pollutant. Plant based material for adsorption and coagulation are widely used method due to high adsorption efficiency and ecofriendly (Sasikala and Muthuraman, 2015). Table 1 shows various types of treatment methods including its advantage and disadvantages.

Coagulation and flocculation is used widely for water and wastewater treatment as treatment step in the surface or ground waters treatment. It is include the removal of heavy metals, anions, color, odor and suspended solids. Coagulation reagent used commonly either from chemical coagulant or natural coagulant. Coagulation is the negatives charges of dissolved and suspended particles in the water will be neutralize by positive charge of the coagulant. After the reaction occurs, the particles will coagulate together where the larger particles or floc will

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Table 1: Advantages and disadvantages of various treatment methods for heavy metals removal (Alfarra *et al*., 2014)

Method	Advantages	Disadvantages
Chemical precipitation	Inexpensive, simple, most metals can be removed	Disposal problem, large amount of sludge produced
Ion-exchange	Metal selective, high regeneration of materials	Fewer number of metal ions removed, high cost
Chemical coagulation	Dewatering, sludge settling	Large consumption of chemicals, high cost
Membrane process and ultrafiltration	High efficiency, less solid waste produced, less chemical consumption	Percentage removal decrease, high initial and high cost
Adsorption using activated carbon	High efficiency, most metals can be removed	No regeneration, high cost, performance depends on adsorbent
Electrochemical methods	Pure metals can be achieved, metal selective, no consumption of chemical	High running cost, high capital cost
Natural coagulation	Toxic free, safe, eco-friendly, low cost	Rarely investigated

quickly settle to the bottom of water supply. Chemical coagulants are added for the removal of dissolved chemical species and turbidity from water such as alum ($AlCl_3$), Ferric Chloride ($FeCl_3$) and Polyaluminium Chloride (PAC). The effectiveness of these chemicals as coagulant is well-recognized (Alfarra *et al*., 2014). Natural plant based coagulant mostly either polysaccharides or proteins. Natural coagulants are water soluble substances, material from vegetable and animal origin. The coagulants contains antimicrobial properties therefore reduce or eliminate the content of microorganism will cause disease and its natural origin ensures that the biodegradability of sludge produced can be used in agriculture and safe for human. Widely used coagulant is synthetic coagulants such as aluminium sulphate, however, it cause many problem therefore an alternative coagulant is more desirable to be a natural coagulant.

Natural coagulants are safe, eco-friendly and toxic free compare with chemical coagulants (Choy *et al*., 2014). Due to its biodegradability and environmental friendly nature, plant based natural coagulants have growing interest among researchers. Many materials of plant origin were studied as a source of natural coagulants (Sanghi *et al*., 2006; The *et al*., 2014). Instead, the natural coagulant also have been successfully used according to the past investigation where water clarification and reduction of microorganism (Pritchard *et al*., 2010) organic matter removal (Bhuptawat *et al*., 2007) and improvement of wastewater microfiltration performance (Katayon *et al*., 2007) by extraction of different plant material as natural coagulant. Polysaccharides behave as polyelectrolytes when charges are present and positively charged groups are ammonium groups while negatively charges groups are carboxylic groups or sulfate groups. The previous studies on Nirmali seeds (Yin, 2010), Moringa Oleifera and Cactus (Saenz *et al*., 2004) show that plant based coagulant capable as natural coagulant. Chitin is the second most abundant polysaccharide in nature and nature polymer that obtained by grinding the shell of shrimps and carbs. However, chitin also can be presence within the plant such as mushroom. Chitin and its derivatives are employed as chelating agent that used for waste water and water treatment by separating organic compounds and heavy metals and in sewage treatment is by precipitating certain anionic wastes and trap pollutant. According to Rinaudo (2006), chitin and its derivatives are applicable in many fields such as food, cosmetics, agriculture, textiles, wastewater treatment and pharmaceutical industries. The extraction of chitin have no effect to the ecosystem and contain all advantages provided by polysaccharides, considered that as the source of chitosan and both are biocompatible biopolymers for animal tissues with low toxicities (Lima and Airoldi, 2004). Due to biodegradability, biocompatibility, non-toxicity nature, the natural bio polymer, chitin and its derivatives have been tried as adsorbent (Karthik and Meenakshi, 2015). Extraction of chitin can be used to produce chitin-derived products such as chitosan, chito-oligosaccharides and glucosamine. Therefore, this study focuses on the extraction of chitin from Petai Belalang for development of natural coagulant. The main objectives of this study are extraction of chitin from matured Petai Belalang peel in different concentration of 1.0, 2.0 and 3.0 M Hydrochloric acid (HCl) and characterizations of both extracted chitin and dried peel sample using FTIR and DSC equipment.

MATERIALS AND METHODS

Sample collection: The matured Petai Belalang peels were collected from locally available source that dried naturally in sunlight to extract chitin. Then, the seeds were separated from the pods. The peels were grinded by using mechanical grinder to convert Petai Belalang into fine powder (Fig. 1).

Dilution of Hydrochloric Acid (HCl): Hydrochloric Acid (HCL) was used for the extraction of chitin. A 1000 mL of diluted hydrochloric solution made by dissolving concentrated HCl (12 M, 36.5 g/mol) and distilled water. Appropriate dilution of the HCl solution was carried out in order to obtain the desired concentration of HCl at 1.0, 2.0 and 3.0 M. The amount of concentrated HCl required to be mix with distilled water are different at each concentration where the calculation based on Eq. 1:

$$M_1V_1 = M_2V_2$$

Fig. 1: Matured petai belalang peel

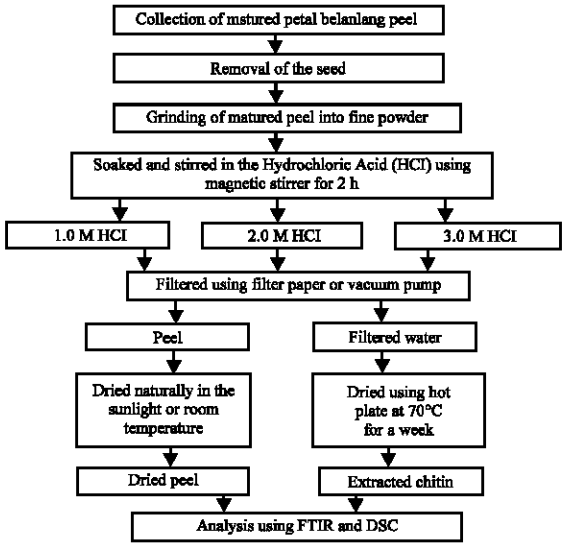

Fig. 2: Flowchart for sample preparation

Preparation of coagulant: About 5 g of the powder sample was taken for the extraction process at 500 mL of different concentration of Hydrochloric Acid (HCl) to determine the chitin content at different concentration. Then, the powder soaked in the diluted hydrochloric acid, 1 M and stirred using magnetic stirrer at 600 rpm for 2 h without heating at room temperature. The sample was then filtered using either filter study or vacuum pump in order to obtain the filtered water and the peel. Both of the filtered water and residues were dried by hot plate at 70°C for a week and in the sunlight or room temperature, respectively. The extracted chitin and the dried peel will be analyzed using FTIR and DSC to determine the chitin in the matured Petai Belalang peel that act as coagulant. The steps will be repeated at 2.0 and 3.0M of Hydrochloric Acid (HCl) (Fig. 2).

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

Extracted chitin: As shown in Fig. 3a, the spectrum of chitin at 1.0 M extraction shows a broad band at 3330 cm^{-1} due to the O-H stretching, NH stretching and hydrogen bonds. The band at 1738 cm^{-1} is assigned to the carbonyl C = O stretching of chitin that attributed to the vibrations proteins band, C = O-NH-CH_3 of amide I band. The sharp band at 1435 cm^{-1} is assigned to the CH_3 group and at 1621 cm^{-1} corresponds of proteins band, C = O-NH-CH_3 to the NH bending of amide II. The vibrations band at 1074 cm^{-1} contribute to C-O-C vibration inside the chitin ring and many peaks produced due to the presence of hydroxide from chitin which contains a single bond C = O (Puspawati and Simpen, 2010). The peak at 778.21 cm^{-1} corresponds to ring stretching band for β-1, 4 glycosidic bonds (Zaku *et al*., 2011).

Figure 3b and c represents another chitin spectrum. The peak at 3330 cm^{-1} corresponding to OH group of chitin is similar to the band in the 3.0 M chitin extraction which indicates that in 2.0 and 3.0 M there are still have good interaction through hydrogen bonding. In Fig. 4b, c, it showed the peak at 779 cm^{-1} which indicated the stretching ring of characteristic band for β-1, 4 glycosidic bonds. Increasing of HCl concentration for chitin extraction shows different results in FTIR analysis either similar or loss the band of chitin polymer. These observations indicate that concentration of HCl for extraction has great effect towards the wave numbers of the chitin content.

Dried peel: From Fig. 4a, the chitin showed peak at 3284 cm^{-1} which corresponds to NH and OH stretching vibration (Zaku *et al*., 2011) and the band at 2918.44 cm^{-1} is attributed to C-H stretching band that converges to OH stretching with N-H. The band at 1620 cm^{-1} is attributed to the N-H bonding deformation of amide 2 while the band that corresponds to the amide 1 stretching of carbonyl group, C = O at 1720.34 cm^{-1} of protein band, C = O-NH-CH_3. The band at 1316 cm^{-1} attributed to deformation of CH_3 group and at 1031 cm^{-1} band is stretching band for C-O-C of glucosamine ring. In Fig. 4b shown slightly different compare to Fig. 4a where the OH stretching vibrations of absorption band at 3303.59 cm^{-1} and absorption peak at 2918.24 cm^{-1} is from C-H vibration. The absorption peaks at 1619 cm^{-1} corresponds to the NH deformation of amide II and the characteristic carbonyl group, C = O stretching of chitin that corresponds to the vibration of the amide I at 1720 cm^{-1} which slightly shorter compare to a. Band at 1309 cm^{-1} corresponds to the CH_3 group is much shorter compare in a and

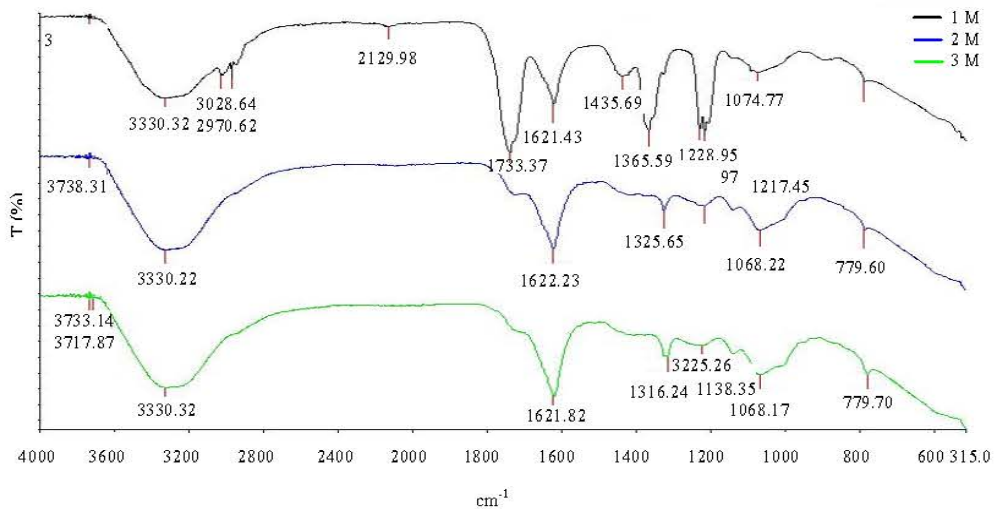

Fig. 3: FTIR analysis for extracted chitin at different of HCl concentration: a) 1.0, b) 2.0 and c) 3.0 M

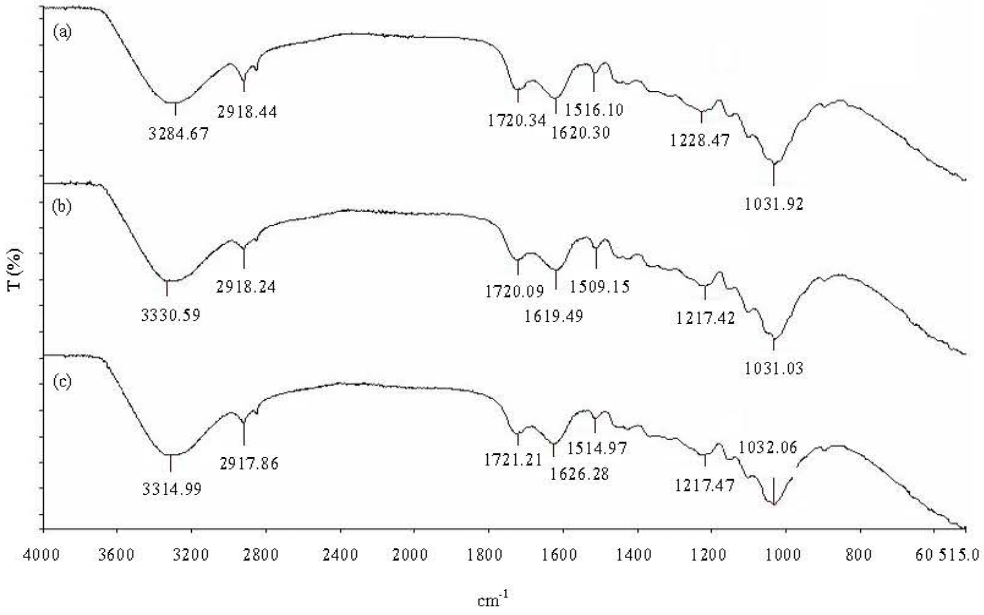

Fig. 4: FTIR analysis for dried peel at different of HCl concentration: a) 1.0; b) 2.0 and c) 3.0 M

C-O-C vibration inside chitin ring showed the vibration band at 1031 cm^{-1} which similar in a. IR characterization in Fig. 4c showed a band located at 3315 cm^{-1} which corresponds to OH stretching vibration. The band which attributed to the C-H vibration of CH_3 is much shorter compare to both in a and b at 2917 cm^{-1}. This band converges to O-H stretching with N-H (Rumengan *et al*., 2014). The band at 1721 cm^{-1} is attributed to the vibrations of the protein group, amide 1 band for the carbonyl C = O stretching of chitin from acetamide ($NHCOCH_3$). Other absorptions bands for the chitin are at 1626 and 1314 cm^{-1} indicating the NH deformation of amide 2, protein band, C = O-NH-CH_3 and deformation of the CH_3 group, respectively. Peak at 1032 cm^{-1} attributed to the C-O-C stretching vibration of the glucosamine ring inside the chitin ring (Rumengan *et al*., 2014).

Differential Scanning Calorimetry (DSC)

Extracted chitin: Figure 5a-c shows the endothermic peaks for chitin in all three different HCl concentrations from dried filtered water. The thermograms shows clearly two peaks of endothermic where the first broad

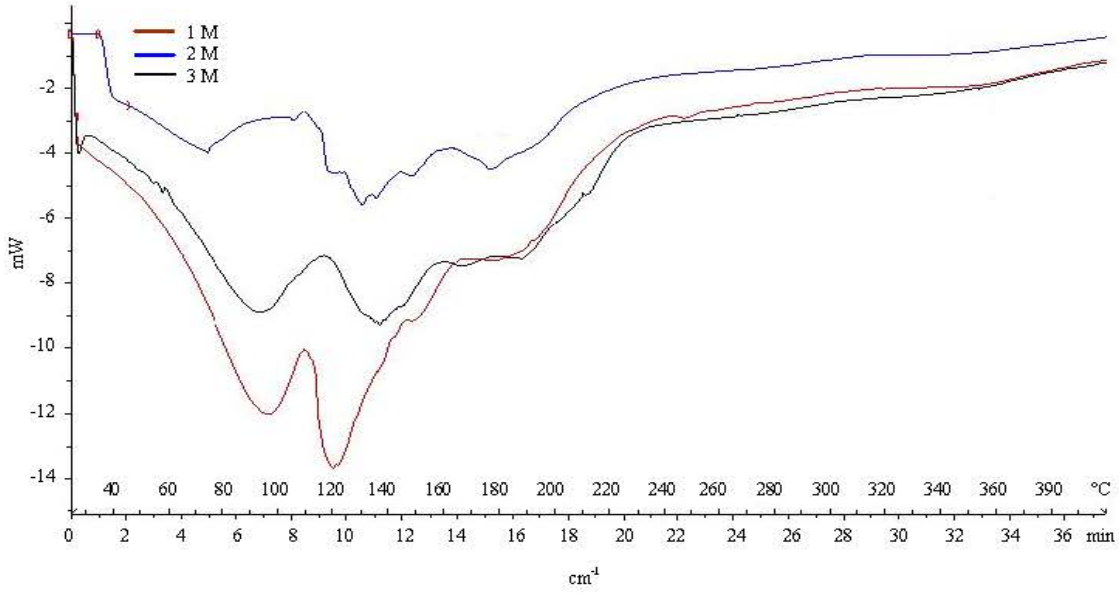

Fig. 5: DSC curve analysis for extracted chitin at: a) 1.0 M; b) 2.0M and c) 3.0M of HCl

endothermic at 1.0, 2.0 and 3.0 M are 94, 74 and 92°C, respectively is representing of moisture and bound water in the sample (Kittur *et al*., 2002) and 51.53, 88.77 and 32.51 J/g sample of polymer was absorbed in the process.

The endothermic peaks showed in the between the room temperature and 95°C which indicating that the presence of crystalline and phase change during heating process. The thermograms above showed the exothermic peaks for chitin extraction is below the decomposition temperature while heating during crystallization of polymer which usually the exothermic peaks that indicate the decomposition of polymer of chitin is approximately up to 360°C (Nam *et al*., 2010).

Second endothermic peaks for 1.0, 2.0 and 3.0 M are 121, 130 and 136°C, respectively is a relaxation endotherm (Olorunsola *et al*., 2015) with enthalpy of 69.73, 72.58 and 29.98 J/g where endothermic relaxation is a second order reaction like glass transition (Horvat *et al*., 2005). Therefore, in other words the higher the peak enthalpy, the denser the crystallinity. This is shows that chitin at 3.0 M has less dense crystallinity as evidenced by lower H at 32.51 and 29.98 J/g for first and second endotherm, respectively compared to the others.

According to Fig. 5, the exothermic peaks that indicate the decomposition of polymer in chitin supposed up to 360°C approximately (Nam *et al*., 2010) do not present in the curve for all concentration. This is due to the aging and matured of Petai Belalang peel used as raw material compared to young peel that may contribute to better result. This is because the matured peel may have loss the polymer content in the peel due to degradation under the sun.

Dried peel: Figure 6 shows the result of thermograms for dried peel that dried at room temperature. In Fig. 6a-c clearly shows two sharp endothermic peaks, the first endothermic peaks for 1.0, 2.0 and 3.0 M is 84.83, 87.04 and 81.11°C, respectively with enthalpy -346.92, -360.35 and -194.15 J/g, respectively due to loss of water. Endothermic peaks were obtained at various temperatures attributing to the evaporation of water and composition of chitin. Second endothermic peaks shows at 148, 156.50°C and 158.25°C, respectively is a relaxation endotherm (Olorunsola *et al*., 2015). Figure 6b-c shows the exothermic peaks for chitin extraction is below the decomposition temperature while heating during crystallization of polymer which usually the exothermic peaks that indicate the decomposition of polymer of chitin is approximately up to 360°C (Nam *et al*., 2010). In Fig. 6a, small exothermic peaks showed at 331.14°C due to the decomposition of N-acetyl (GlcNAc) units which is the main group in the chitin (Nam *et al*., 2010). The DSC curve on Fig. 6a, show small exothermic peaks at 331.14°C which indicated the decomposition of polymer while in Fig. 6b-c, the exothermic peaks do not present in the curve. Based on the observation, at low concentration of 1.0 M solution show the exothermic peaks and at high concentration of 2.0 and 3.0 M the exothermic peaks disappear in the curve. This is because the low content of polymer in the aging and matured peel causes the polymer is easy to completely dissolve in the high concentration solution.

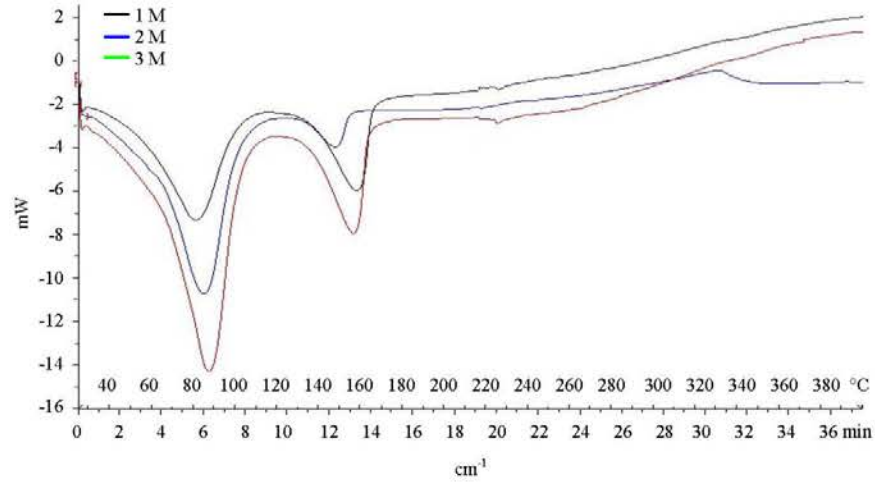

Fig. 6: DSC curve analysis for dried peel at: a) 1.0 M; b) 2.0 M and c) 3.0 M of HCl

CONCLUSION

The study indicated that the natural coagulant can be developed from matured Petai Belalang peel by the extraction of chitin using hydrochloric acid. Chitin has a potential as coagulant and flocculant and able to evaluate economical use of natural coagulant. The IR spectra of extracted chitin in 1.0 M solution gave a characteristic of protein band, C = O-NH-CH_3 that corresponds to the NH bending of amide 2 and carbonyl C = O stretching of amide 1 at 1621 and 1738 cm^{-1}, respectively. OH bond, NH and C-H stretching was also detected at 3330.8, 3028 and 2970 cm^{-1}, respectively. Characterization of chitin using FTIR analysis showed that the extracted chitin in 1.0 M corresponds to α-chitin formation. From the result of DSC analysis, it showed two endothermic peaks in all concentration for both extracted chitin and dried peel whereas exothermic peaks is presence in 1.0 M solution for dried peel only. This can be concluded that due to the aging peel used as a raw material it lead to bonding ruptured and degradation of chitin polymer under the sun and caused the polymer to dissolve completely in high concentration. Last but not least, it can be concluded that 1.0 M solution is good and suitable for chitin extraction in the development of natural coagulant from matured Petai Belalang peel.

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