ARTICLE REVIEW; UTILIZATION OF CRAB SHELLS FOR NATURAL COAGULANT/ADSORBAN MATERIALS

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ABSTRACT

This article aims to review the use of rajungan shells as a natural ingredient for coagulants/adsorbans. Based on the results of literature studies show that crab shells, waste from the freezing and canning industry of crab meat can be further processed into chitosan. This chitosan product can be used as a natural coagulant / adsorban. Chitosan extracted from crab shells as natural coagulants/adsorbans is applied in water purification, silicon purification and waters polluted with heavy metal Pb.

Keywords : *Chitosan, Heavy metal, Freezing, Canning, Purification*.

INTRODUCTION

Based on the Indonesian Government Regulation No. 18/1999 Jo.PP 85/1999, waste is defined as the residue or waste of a business and or human activity. Waste is generated from various sources including industry, households, hospitals, mining, agriculture and plantations, fisheries, transportation, etc. One of the wastes from the fishing industry is crab shells. This material is produced from the crab meat freezing and canning industry.

Currently, crab is a leading export commodity for Indonesian fishery products, especially for exports to Japan, the European Union, and the United States. The increasing demand for exports has an impact on the volume of crab production which continues to rise. The increase in production will be followed by an increase in the amount of waste produced, both solid waste in the form of shells and liquid waste in the form of boiled water.

In one crab produces process waste consisting of 57% shell, 3% *body reject*, and 20% boiled water. Crabs weighing 100-350 grams, produce crab shell waste between 51-150 grams. The increase in crab shells will have an impact on environmental pollution if left untreated. The use of crab shells is a solution in overcoming the problem of environmental pollution and one of the efforts to reduce the volume of waste that continues to increase.

According to Marliani (2014), the existence of waste can certainly have a negative impact on the environment, especially for human health, so it is necessary to handle waste. The degree of danger of poisoning posed by waste depends on the type and characteristics of the waste itself. Waste that is deliberately disposed of into the environment without being handled first can result in pollution, both in rivers, land and air (Indrianeu and Singkawijaya 2019). The existence of waste also affects the condition of the quality of a water which decreases along with the many human activities that produce liquid waste, both industrial and household. The presence of this waste can cause unpleasant odors and tastes and disturb the surrounding ecosystem (Agustira and Lubis 2013).

In general, crabs are only used for consumption, while the shells, both legs, carapaces and claws, are simply thrown into waste without further processing or other uses. Crab shells can be used for coagulant material because in the crab shell there are chitin compounds. According to Kadzim *et al.* (2020), crab shells contain organic compounds consisting of 30-40% protein content, 30-50% mineral content, and 20-30% chitin content. The results of research by Lubena *et al.* (2020) inform that crab shells contain protein of 29.91%, ash content of 44.03% and moisture content of 0.45%.

Chitin can be further converted into chitosan. According to Putri *et al.* (2020) chitosan is a chitin-derived polymer compound that has removed its acetyl group leaving a free amine group. Chitosan has the ability as a coagulant because it has a lot of nitrogen content in the amine group. Amine and hydroxyl groups make chitosan more active and polycationic, these properties are used as coagulants. This article aims to review the use of rajungan shells as a natural ingredient for coagulants.

CHITOSAN EXTRACTED FROM CRAB SHELLS

Chitosan extraction from the shell of the farm is carried out through 4 stages, namely deproteination, demineralization, depigmentation, and deacetylation. The yield and quality of chitosan from crab shells vary depending on the type and concentration of the solvent and the extraction temperature used.

Several research results have been reported to be related to chitosan amendments from the results of the extension of the platform shell. Natalia *et al.* (2021) reported chitosan yield from crab shells of 13.37%, the extraction process was carried out at room temperature. Setha (2019) in his research producedan chitosan of 5.12 – 5.63%. Lalenoh (2018) 4.9%, Nadia *et al.* (2018) 17.39%; Cahyono (2015) 14%; Ariesta (2007) 23.13%. The success of the chitosan manufacturing process can be measured by the resulting amendment value. Cahyono (2015) also stated that the efficiency and effectiveness of an extraction of raw materials in the manufacture of chitosan can be seen from the value of the amendment.

The quality of chitosan extracted from crab shells is reported to meet Indonesian national quality standards as researched by Natalia et al (2021). The quality of chitosan is as shown in Table 1.

Table 1. Chitosan Quality of Ecstasy Result of Crab Shells

Parameter	Quality of EFSA chitosan	Quality of chitosan SNI	Chitosan from crab shells
Color	-	Light brown to white	Yellowish white
Water (%)	≤ 10	≤ 12	11.25 – 12.93
Ash (%)	≤ 3	≤ 5	1.62 – 1.75
Nitrogen (%)	≤ 6	≤ 5	5.12 – 5.45
Lipid	≤ 1	-	0.25 – 0.49
Viskositas (cPs)	-	-	37.50 -38.33

Source: Natalia *et al.* (2021)

Chitosan in general has biological and chemical properties. According to Hambali *et al.* (2017) the biological properties of chitosan are natural, biodegradable, safe and non-toxic polymers. Its chemical properties are high-density cationic polyamines, reactive amino/hydroxy groups, high molecular weight, high charge linear polyelectrolytes at a pH of less than 6.5, chelates of some transitional metals and are easily chemically modified.

Chitosan is only soluble in dilute acids, such as citric acid, formic acid, acetic acid, unless the substituted chitosan can dissolve with water. The carboxyl group in acetic acid will facilitate the dissolution of chitosan because there is a hydrogen interaction between the amine group of chitosan and the carboxyl group. The solubility of chitosan is influenced by the duration of deacetylation with NaOH and its temperature. Acetic acid is one of the weak acids of the carboxylic acid group that has a carboxyl group (-COOH). In acidic solutions, the free amine group is well suited as a polycationic for forming dispersions or chelating metals. Therefore, chitosan in acidic solutions becomes polymers with a straight structure so that it is useful for flocculation, immobilization of enzymes or film-forming. The chitosan-free amine group in the acidic atmosphere will be protonated to form a cationic amino group (NH3 +).

CHITOSAN EXTRACTION RESULTS OF CRAB SHELLS AS NATURAL COAGULANTS / ADSORBANS

Coagulants are compounds that have the ability to destabilize colloids by neutralizing electric charges so that colloids can combine to form microflocs so that they easily precipitate. Natural coagulants are less harmful to the environment compared to synthetic coagulants (Hambali *et al.* 2017). Excessive and continuous use of synthetic coagulants will have a negative impact due to the increasing amount of sludge volume and can accumulate in the human body. One such natural coagulant is chitosan. Sendotian coagulants that are often used are Alum (AL2 (SO4)3), Sodium Aluminat (NaALO 2), Feri Sulfate (Fe2 (SO4)3), Ferrous Sulfate (FeSO4), Fero Chloride (FeCI2) and Ferry Chlorida (FeCI3).

Chitosan has several properties that make it a coagulant and/or flocculant to remove contaminants under dissolved conditions. Chitosan has a high cationic charge, and binds the aggregate and precipitates it under neutral or alkaline pH conditions. In addition, chitosan also has non-toxic and biodegerable properties, as well as the ability to chelat metals, as well as particulates and dissolved compounds (Hambali *et al.* 2017).

The working principle of chitosan as a coagulant is the interaction of cation polyelectrolytes contained in coagulants with colloidal particles contained in liquid waste (samples) by forming bridges between particles. Colloidal particles in water (samples) are usually negatively charged. The positive charge of chitosan will neutralize the negative charge of colloidal particles so that it will form flocs that will be easy to precipitate.

Chitosan has the effect of drastically reducing the repulsion between colloidal particles, which allows van der Waals to occur attraction forces, thereby triggering colloidal agglomeration and suspended fine particles forming microfloc. Particles are coagulated, tend to glue strongly, and settle quickly. If too much chitosan is used, a charge reversal can occur and the particles will split/re-spread. Therefore, the concentration of chitosan added to the coagulation process must be given appropriately. The mechanism of coagulant compounds in the process of quagulation schematically as shown in Figure 1.

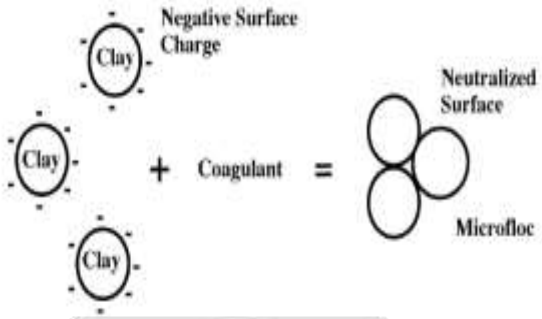

Figure 1. Coagulation mechanisms (Source : Pillai 1997 in Hambali *et al.* 2017)

Chitosan as a coagulant has been applied as a water purifier as research has been carried out by Lubena *et al.* (2020). The results of his research show the following: 1) The highest Fe reduction level was obtained at a stirring time of 15 minutes, with the addition of 5% chitosan to the sample water where the Fe level went from 10.67mg/l to 2.01mg/l with a percentage of Fe levels of 81.13. 2) The highest turbidity reduction was obtained at a stirring time of 15 minutes, with the addition of 5% chitosan to the sample water where the turbidity decreased from 8.91 NTU to 0.78 NTU with a percentage decrease in turbidity of 91.29%. 3) The decrease in Fe levels with the use of chitosan biocoagulants from the shell of the flatbed obtained better results than alum. At a stirring time of 15 minutes and an addition of 5%, the addition of alum resulted in a decrease in Fe levels of 75.33% and in the addition of chitosan biocoagulants obtained better results with a decrease in Fe levels of 81.13%. 4) The decrease in turbidity in the addition of chitosan biocoagulants obtained better results than alum. At the time of stirring 15 menit and the addition of 5% alum turbidity decreased from 8.91NTU to 3.26 NTU with a percentage decrease of 63.37, while in the use of chitosan biocoagulants turbidity decreased from 8.91 NTU to 0.78 NTU with a turbidity unan percentageof 91.29 %. 5) The use of chitosan biocoagulants from the shell of the flatbed is very effective as a coagulant, as evidenced by the decrease in Fe levels and the signifying turbidity of the fish. Meanwhile, the addition of the percentage of coagulants has no effect on the pH value

Another application of chitosan crab is as a metal absorber as reported by Yuliusman and Adelina P.W (2010). Chitosan can bind heavy metals by using the principle of coagulation. The principle of chitosan coagulation is an ion exchanger in which amine salts formed due to the reaction of amines with acids will exchange protons belonging to polluting metals with electrons owned by nitrogen (N). The process of coagulation of heavy metals by kitosan can be seen in Figure 2.

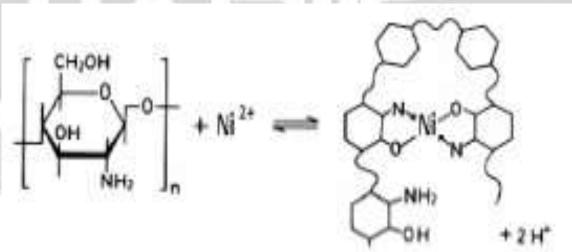

Figure 2. Binding of metal ions by chitosan (Source : Yuliusman and Adelina P.W 2010)

According to Yuliusman and Adelina P.W (2010) chitosan has an excellent in adsorbing metal nicles under optimum conditions. Optimum con of adsorption by chitosan at pH 3, solid/liquid ratio of 1:100, and contact time of 30 minutes. While the optimum condition of desorption is obtained at pH 2 and contact time 60 minutes.

Chitosan extracted from crab shells is also used to clean silicon from impurities of iron and manganese ions. Silicon used for solar cells requires a very high purity above 99.99%. Silicon used for semiconductor and solar cell purposes is taken from the result of the separation of Si and O. Silicon is obtained from quarry sand mining. Quartz sand from Indonesia contains impurities of the elements Al, Fe, Ca, Mg, Ti and others that form complex bonds with SiO2 compounds. One of the ways that can be done to purify silica from quartz sand to be free from impurities is adsorption with chitosan through the principle of coagulation. The results of Pitriani's research (2010) show that chitosan from rajunga shells can be used to purify silicon from impurities of iron and manganese ions. The optimum material of chitosan is 0.5 grams to be able to adsorb Fe ions by 59.09% and Mn by 51.69%. The optimum contact time of adsorption of Fe (72.07%) and Mn (52.50%) ions was 30 minutes.

The optimum pH of adsorption of Fe (77.68%) and Mn ions (58.67%) occurs at pH 3. The optimum temperature of adsorption of 85.39% Fe ions is 70 o C , while for adsorption 65.72% Mn ions are 60^{o} C.

Chitosan from crab shells can also be used to absorb lead ions. The presence of lead ions in the aquatic environment is very dangerous because it is toxic at certain concentrations. This pb ion is bioaccumulative because it cannot be digested by biota both low-level and high-level biota. The results of research by Supriatin *et al.* (2018) inform that theabsorption rate of chitosan with concentrations of 1, 2, 4, and 8% respectively is 8.09; 36.26; 45.42 and 57.47 % with a stirring time of 30 minutes. The higher the concentration of chitosan used, the higher the adsorption power value of lead heavy metal (Pb) levels.

CONCLUSION

Crab shells, waste from the freezing and canning industry of crab meat can be further processed into chitosan. This chitosan product can be used as a natural coagulant / adsorban. Chitosan extracted from crab shells as natural coagulants/adsorbans is applied in water purification, silicon purification and waters polluted with heavy metal Pb.

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