CHITO-CHITO: CHITOSAN AS TURBID-COLOR ADSORBENT ON "*TEMPE*" INDUSTRIAL WASTEWATER

Muhamad Alfiyan Zubaidi[1]*, Hamasyah Hamzah Mumtaza[2], Rimo Hasnan[3]

(Bogor Agricultural University, Jl. Raya Darmaga Kampus IPB Darmaga Bogor 16680, West Java, Indonesia) [1]Faculty of Agricultural Engineering, Department of Food Science and Technology, Bogor Agricultural University, Indonesia.
[2]Faculty of Fisheries and Marine Science, Department of Aquatic Product Technology, Bogor Agricultural University, Indonesia.
[3]Faculty of Agricultural Engineering, Department of Mechanical and Bio-system Engineering, Bogor Agricultural University, Indonesia.

*Corresponding author: Muhamad Alfiyan Zubaidi, +6285657380526, alfiyan1994@gmail.com

Keywords: Chitosan, adsorbent, *tempe* wastewater, fisheries waste

ABSTRACT

Citeurep is *tempe* industrial center in Bogor, consisting of 300 crafters. *Tempe* industry will produce waste 3000-5000 liters/ton of products [1]. *Tempe* wastewater has TDS (25,060 mg/l), TSS (4,012 mg/l), pH (4.16), *temp*erature (75ºC), NH3N (26.7 mg/l), BOD (31,380.87 mg/l) and COD (35,398.87 mg/l) and has turbid/brown color which has passed the quality standard for environmentally safe waste [2]. Fisheries industry in Indonesia reached 5.3 million tons/year that will produce wastes such as shrimp shells which reached 65%-85% of the mass [3][4]. Shrimp shells can be processed into chitosan as an effective adsorbent for reducing aquatic-pollutant using Suptijah methods [5][6]. The results showed that chitosan has good performance at pH 6.6 to 6.8 and 175-225 ppm. In these conditions, chitosan can lower the value of 94.33%-95.17% turbidity, TSS 95.10%-95.82%, BOD 72.09%-79%, COD 76.72%-79.40%, TKN 12.50%-27.82%, NH3 80.84%-82.56%, NO2-N 47.69%-54.74%, NO3-N 19.39%-40.14% [7].Thus, addition chitosan on *tempe* wastewater before disposal can reduce environmental pollution.

INTRODUCTION

Indonesia is an agricultural country with a population growth rate reached 1.56% annually [8]. The high population growth in Indonesia, led to an increase in the need for food to meet the nutritional needs of the Indonesian people. Soy is one of chosen food by Indonesian people to meet the vegetable protein. Indonesia needs two million tons of soybeans per year until 2008. 1.2 million tons of soybeans consumed as *tempe* and 0.8 million tons of soybean as another processed food with soy consumption growth rate reaches 7.22 % per year [9]. Thus, the *tempe* production will be produced harmful waste 3000-5000 liters/tons product [1]. It means, Indonesia will produce 3.6-6.0 billion liters of *tempe* wastewater every year with the addition of waste volume up to 0.43 billion liters per year.

The *tempe* wastewater has passed the quality standard for environmentally safe waste and harmful for the environment [2]. The waste has *temp*erature 75º C that can damage aquatic habitats. The content of TDS (Total Dissolve Solid) reached 25.060 mg/l, TSS (Total Suspended Solid) reached 4.551 mg/l , pH 4.16 , BOD (Biological Oxygen Demand) reached 31,380.87 mg/l and COD (Chemical Oxygen Demand) reached 35,398.87 mg/l.

On other hand, Fisheries industries in Indonesia has produced waste up to 5.3 million tons/year [10]. The high abundance of the fisheries wastes must be utilized especially in reducing the negative effects of *tempe* wastewater. Fisheries wastes treatment primarily of chitin from shrimp shells that reached 65-85 % of the total mass can be modified to chitosan and used as pollutant adsorbent in *tempe* waste water to makes it safe to be discharged into the environment [3][4].

RESEARCH METHOD

In this research is used meta-analysis method. Its refers to methods that focus on contrasting and combining results from different studies, in the hope of identifying patterns among study results, sources of disagreement among those results, or other interesting relationships that may come to light in the context of multiple studies.

TEMPE WASTEWATER

Tempe is one of favorite food for the Indonesian people with the level of consumption reached 1.2 million tons annually [9]. The high demand for *tempe* would also increase *tempe* waste water that harmful for the environment.

Table 1: The Content Analysis Results of *Tempe* Liquid Waste Water

No.	Parameter	Unit	Standard Safe Waste Water Quality	Liquid from Stew Soybean (Average)	Liquid from Immersion Soybean (Average)
1.	*Temp*erature	^{0} C	45	**75**	32
2.	TDS (Total Dissolve Solid)	mg/l	5.000	**25.060**	**25.254**
3.	TSS (Total Suspended Solid)	mg/l	500	**4.012**	**4.551**
4.	pH	-	5 - 9	6	**4,16**
5.	NH_3N	mg/l	20	16,5	**26,7**
6.	NO_3N (Nitrate)	mg/l	50	12,52	14,08
7.	BOD (Biological Oxygen Demand)	mg/l	300	**1.302,03**	**31.380,87**
8.	COD (Chemical Oxygen Demand)	mg/l	600	**4.188,27**	**35.398,87**

Source: Wiryani, Erry. *Analisis Kandungan Limbah Cair Pabrik Tempe*. Semarang: Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Diponegoro.

Based on Table 1. The wastes potential to contaminate the surrounding water environment. *Tempe*rature of liquid wastes derived from boiled soybeans reached 75^{O}C, it will endanger the lives of aquatic organisms. The optimum *tempe*rature for the living things in water is 25-30^{0}C. River water *tempe*rature rise will disrupt the lives of animals and plants because water dissolved oxygen levels will drop along with the *tempe*rature rise [11]. Plants will stop growing at water *tempe*ratures below 10^{0}C or above 40^{0}C. There is a reciprocal relationship between dissolved oxygen and the rate of breathing creatures live. Rising *tempe*ratures will lead to increased respiratory rate and decreased mortal dissolved oxygen in the water. The rate of decline in dissolved oxygen (DO) caused by organic waste will be faster because of the increased pace of breathing creatures higher [12].

Wastewater from the process of boiling and soaking soybeans, has a value of TDS and TSS were far beyond standard effluent quality standard. Effect of suspended solids (TSS) and dissolved solids (TDS) varies, depending on the chemical nature of the suspended material nature. Harmful effects on fishes, zooplankton and other creatures in principle is clogging the gills by particles that cause affixation. Besides, it also have an effect on fish behavior and the most common is a rejection of the murky water , ate barriers as well as increased search of shelter. Patterns found in rivers that receive most of the suspended solids, in general is the reduced number of species and number of individual living beings [12].

Acidity of wastewater from soybean water quality standard has been exceeded standard. Waste water and effluents from industrial activities are discharged into waters will change the pH of the water, and may affect aquatic organisms. Normal water are eligible for life has a pH ranging between 6.5-7.5 [11]. Waste from *tempe* production is included in the biodegradable waste that can be destroyed by microorganisms. Organic compounds contained in it will be destroyed by the bacteria even though the process is slow and often accompanied by the release of a foul odor. Ammonia concentration of 0.037 mg/l was able to cause the stinging smell of ammonia. In domestic waste, most of the organic nitrogen is converted to ammonia in anaerobic decay and become nitrate or nitrite on aerobic spoilage [13].

Tempe waste water turned out to nitrate is below the threshold, but the free ammonia from waste soy marinade has exceeded the threshold, it can certainly harm the marine environment. Biodegradable waste material is a nutrient for aquatic plants [14]. Biodegradable waste ingredients high in water can cause eutrophication that results in a population of some plants blooming water such as Algae , Phytoplankton and Water Hyacinth (*Eichhornia crassipes Solm*) [11]. Lead to an increase in local benthic eutrophication dissolved oxygen shortage will widen. This can reduce the amount of suitable habitat for fish and can cause a decrease in the overall number of fish [12].

Values of Biological Oxygen Demand (BOD) of the effluent is so high that the amount of oxygen required by microorganisms to degrade in the waste waters is very large. Organic materials will be broken down by microorganisms into CO_2, H_2O and NH_3 gases. NH_3 gas is causing foul smell. Likewise, the number Chemical Oxygen Demand (COD) is very high so it will require a very large oxygen so the waste can be oxidized through chemical reactions. In this case the organic waste will be oxidized by *potassium bichromate* ($K_2Cr_2O_7$) gas into CO_2 and H_2O and chromium ions [11]. The wells of water used in the process of making this *tempe* has criteria still meet water quality standards of class B, which is colorless, tasteless and odorless normal as well as turbidity, dissolved solids and pH are still health qualify .

CHITOSAN

Chitosan is a natural resin that can be made from the skin, head and leg shrimp. Moreover chitosan is derived from chitin which is a natural polymer found in shrimp shells or waste about 10% -25%. Chitosan is derived from chitin modified chitin *diacetylation*. These compounds can be processed and used as absorbent material heavy metals generated by industrial waste. Chitosan is a natural polymer that is non- toxic, environmentally friendly and more easily degraded naturally. The nature and function of chitin and chitosan are very diverse. Chitin is very prominent in his ability as an absorbent, whereas chitosan stands out in its ability as a binding or chelating the coagulation and flocculation process, but it also serves as a stabilizer, thickener, filler, pen-gels, films and other packaging, so much needed in the industry drugs, cosmetics, food, paints, adhesives, paper, sewage treatment, fertilizer and others [15].

One of the utilization of shrimp shells is to be processed into chitosan. Chitosan is a cationic polyelectrolyte and polymer chain length, has a large molecular weight and reactive because of the amine and hydroxyl groups that act as electron donors. Because of the properties, chitosan can interact with colloidal particles contained in the waste water through a process of bridge between flock particles (coagulation) [16]. The turbidity of waste water was able to reduce by adding chitosan as a coagulant [17]. Long molecular chains of chitosan is able to trap particles suspended in solution and makes agglomeration, thereby functioning as a coagulant [16].
Chitosan has the properties of a good soak and agglomerate. These compounds can be used as an absorbent material heavy metals generated by industrial waste including waste from the printing industry [18].

Manufacture Of Chitosan

A. Manufacture chitin

Deproteination
This process is carried out at a *tempe*rature of 60-70° C using a 1 M NaOH solution with shrimp powder with NaOH ratio = 1:10 (g powder / ml NaOH) while stirring for 60 minutes . Then the mixture was filtered to separate the sediment taken.

Washing and drying
Sediment washing is done by using distilled water until neutral pH. Then filtered and dried sediment to be taken.

Demineralization
Mineral removal is done at a *tempe*rature of 25-30 ° C using 1 M HCl solution with a ratio of the sample with a solution of HCl = 1:10 (g powder / ml HCl) while stirring for 120 minutes . Then filtered to take sediment.

Decoloration
Demineralized sediment extracted with acetone and be bleached with 0.315 % NaOCl (w / v) for 5 min at room *tempe*rature. Comparison of solid and solvent 1:10 (w / v)

Washing and drying
Sediment washing is done by using distilled water until neutral pH. Then filtered, and the precipitate dried

B. *Deacetylation* of chitin into chitosan

Chitin that has been generated in the above process included in the NaOH solution with a concentration of 20, 30, 40, 50 and 60 % (by weight) at a *tempe*rature of 90-100°C, while stirring constant speed for 60 minutes. The result is a slurry was filtered, the precipitate was washed with distilled water and then added that dilute HCl pH neutral and then dried. Then formed chitosan. Furthermore chitosan were analyzed using FTIR method to determine the degree of *deacetylation* (DD). Powder samples in KBr pellets were made later determined spectrum [19].

USING CHITOSAN

Processed fisheries waste in the form of chitin into chitosan can be used as an absorbent to lessen environmental pollution due to *tempe* wastewater. It also will double impact on utilization of fishery waste that is not has benefit. The main pollutant in *tempe* wastewater will be minimized by the addition of chitosan powder as much as 175-225 ppm and adjust pH between 6.6-6.8 to obtain the most effective of chitosan adsorbent.

Visually, *tempe* waste water has brownish liquid resulting from suspended particles such as proteins and fats. These particles are able coagulated by [16]. Suspended particle coagulation of *tempe* wate water processed will produce translucent color. Besides a result of the suspension of protein and fat, brown liquid waste *tempe* also due to suspended materials such as sand, silt, organic matter, inorganic and other microscopic materials causes the increasing in effluent turbidity values [6]. Further *Dunnett's* test gives the best results for turbidity impairment waste up to 95.17 % with chitosan concentration of 200ppm [6].

Turbidity of the waste is also caused by the value of total suspended solids (TSS). Suspended solids are matters that cause turbidity of the water, insoluble and does not precipitate directly. Suspended solids composed of particles smaller size and weight of the sediment, such as clay, certain organic materials and certain cells of microorganisms. *Dunnett's* test further stated that mixing chitosan with a concentration of 200 ppm would reduce TSS up to 95.82% [6]. It means that the value of the original TSS reached 4,551 mg/l will be reduced to 190.23 mg/l.

Other contaminants indicator is the value of BOD (Biochemical Oxygen Demand). Higher the BOD value indicates that water quality is getting worse. Further *Dunnett's* test results with chitosan treatment concentration value of 200 ppm would reduce BOD by 75 % means that the original content of effluent BOD *tempe* reached 31,380.87 mg/l will drop to 7,854.21 mg/l, whereas for liquid waste from soy marinade will reduce BOD values up to 327.00 mg/l. COD (Chemical Oxygen Demand) is also an indicator of water pollution, the higher the COD value indicates that the water contains a lot of organic materials and inorganic. Further *Dunnet's* test showed that the addition of chitosan with COD concentration of 200ppm would reduce up to 79.40 %, Mean COD will decrease up to 7291 mg/l.

Total value *Kjehdahl* Nitrogen / TKN, the method of analysis to identify the amount of organic nitrogen contained drafts of the materials in the form of protein, ammonia, nitrite and nitrate [20]. The addition of chitosan with 225 ppm concentration will reduce TKN values up to 27.82 %, 82.56% ammonia, 54.74% nitrite and 40.14% nitrate. The nitrogen content would be harmful to the environment and health if the water content exceeds safe limits.

CONCLUSION

The results showed that chitosan has good performance at pH 6.6 to 6.8 and 175-225 ppm. In these conditions, chitosan can lower the value of 94.33%-95.17% turbidity, TSS 95.10%-95.82%, BOD 72.09%-79%, COD 76.72%-79.40%, TKN 12.50%-27.82%, NH_3 80.84%-82.56%, NO2-N 47.69%-54.74%, NO3-N 19.39%-40.14% [7].Thus, addition chitosan on *tempe* wastewater before disposal can reduce environmental pollution.

ACKNOWLEDGEMENT

Thanks to Ibu Pipih Suptijah who help us to finish this research as our advisory. Thanks to ACA2013 committees and thanks to everyone who contribute in this research.

Poster paper

REFERENCES

1. Natalia.(2008). *Analisis Internalisasi Biaya Pengolahan Limbah.* Bogor: Fakultas Pertanian Institut Pertanian.
2. Wiryani, Erry. *Analisis Kandungan Limbah Cair Pabrik Tempe*. Semarang: Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Diponegoro.
3. [DKP]. Departemen Kelautan dan Perikanan. (2000). Laporan tahunan produksi ikan Indonesia. Jakarta: Departemen Kelautan dan Perikanan.
4. Nendes, Maikel. (2011). *Kemampuan Kitosan Limbah Cangkang Udang sebagai Resin Pengikat Logam Tembaga (Cu)*. Padang: Fakultas Teknik Universitas Andalas.
5. Dutta, PK , Joydeep D and Tripathi VS. (2004). Chitin and Chitosan: Chemistry, Properties and Applications. *Journal of Scientific & Industrial Research*. January, vol. 63 (pp 20-31).
6. Suptijah PE, Salamah H, Sumaryanto S, Purwaningsih S, Santoso J. (1992). *Pengaruh berbagai isolasi khitin kulit udang terhadap mutunya [laporan penelitian]*. Bogor: Jurusan Pengolahan Hasil Perikanan, Fakultas Perikanan, Institut Pertanian Bogor.
7. Ibrahim, B, Pipih S, Prantommy. (2009). *The Utilization of Chitosan on Fishery Industrial Wastewater Treatment.* Bogor: Fakultas Pertanian Institut Pertanian Bogor.
8. [BPS]. Badan Pusat Statistik (2008). Data pertumbuhan penduduk Indonesia. Jakarta: BPS.
9. [DKP]. Departemen Kelautan dan Perikanan. (2008). Laporan tahunan produksi ikan Indonesia. Jakarta: Departemen Kelautan dan Perikanan.
10. [DKP]. Departemen Kelautan dan Perikanan. (2004). Laporan tahunan produksi ikan Indonesia. Jakarta: Departemen Kelautan dan Perikanan.
11. Wardhana, W.A. (2004). Dampak Pencemaran Lingkungan.Yogyakarta: Penerbit Andi
12. Connell, D.W. dan G.J. Miller. (1995). Kimia dan Ekotoksikologi lingkungan. .Jakarta: UI Press.
13. Mahida , U N. (1986). Pencemaran Air dan Pemanfaatan Limbah Industri. Jakarta: CV Rajawali.
14. Prawiro, R. (1988). Ekologi Lingkungan Pencemaran. Semarang: Satya Wacana.
15. Knorr D. (1991). Recovery and Utilization of Chitin and Chitosan in Food Processing Waste Management in Food Technology 45, 114-122
16. Chung GH, Kim BS, Hur JW, No HK. (1996). Physicochemical properties of chitin and chitosan prepared from lobster shrimp shell. *Korean Journal Food Science Technology* 28:870–876.
17. Yunizal. (1998). Efektifitas Khitosan sebagai Koagulan untuk Membersihkan Limbah Pengolahan Ikan. *Buletin Teknologi Hasil Perikanan*. 5(1): 7-9
18. Hargono. (2007). *Pembuatan Kitosan dari Kulit Udang Untuk Mengadsorbsi Logam Tembaga (Cu2+).* Jurnal Teknik Kimia. Semarang: Universitas Diponegoro.
19. Hanafi M, Syahrul A, Efrina D, dan B Suwandi. (1999). ”*Pemanfaatan Kulit Udang untuk Pembuatan Kitosan dan Glukosamin*”, LIPI Kawasan PUSPITEK, Serpong.
20. Islam MdS, Khan S, Tanaka M. (2004). Waste loading in shrimp and fish processing effluents: potential source of hazards to the coastal and nearshore environments. Marine Pollution Bul49:103–110. Park E, Enander R, B