NOTE

APPLICATION OF CHITOSAN FROM *Peneaus monodon* AS COAGULANT OF Pb(II) IN WASTE WATER FROM TOLANGOHULA SUGAR FACTORY KABUPATEN GORONTALO

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ABSTRACT

The aim of this research is to remove Pb(II) from waste water of Tolangohula sugar factory, Gorontalo. In this study, coagulation technique was developed using chitosan as coagulant. Chitosan was obtained from Peneaus monodon shell. The effect of coagulant mass was studied by varying the mass of chitosan: 0, 2.5, 5, 7.5 and 10 g. In addition, effect of pH was also examined by varying the pH of solution: 2, 6, 7, 8, 9 and 10. The results showed that the utilization of 10 g chitosan gave the optimal Pb(II) removal of 72.36% or 22.28 x 10^{-6} mg/g. Additionally, Pb(II) removal was optimum (83%) or 25.44 x 10^{-6} mg/g at pH 9. It could be concluded that chitosan coagulant had the ability to adsorb the Pb(II) in the waste water from Tolangohula sugar factory Kabupaten Gorontalo.

Keywords: *Chitosan; Peneaus Monodon; Coagulation; Plumbum*

ABSTRAK

Penelitian ini bertujuan untuk menghilangkan Pb(II) dalam air limbah pabrik gula Tolangohula Kabupaten Gorontalo. Dalam studi ini, teknik koagulasi dilakukan dengan menggunakan kitosan sebagai koagulan. Kitosan diperoleh dari Peneaus monodon. Pengaruh massa koagulan dilakukan dengan memvariasikan massa kitosan 0, 2,5, 5, 7,5 dan 10 g. Selain itu, pengaruh pH juga diteliti dengan memvariasikan pH larutan: 2, 6, 7, 8, 9 dan 10. Hasil penelitian menunjukkan bahwa penggunaan 10 g kitosan memberikan efisiensi penurunan Pb(II) yang optimal sebesar 72,36% atau 22,28 x 10^{-6} mg/g. Selain itu, penurunan Pb(II) yang optimal berada pada pH 9, sebesar 83% atau 25,44 x 10^{-6} mg/g. Dapat disimpulkan bahwa koagulan kitosan memiliki kemampuan untuk mengadsorpsi Pb(II) dalam air limbah pabrik gula Tolangohula Kabupaten Gorontalo.

Kata Kunci: *Kitosan; Peneaus Monodon; Koagulasi; Timbal*

INTRODUCTION

Gorontalo industrial development may give either positive or negative impacts to community and environment. One of negative impacts is environmental contamination. This is mainly due to industrial waste discharged from factories which contains dangerous and poisonous materials [1].

One of the most dangerous pollutants is lead, which exists as cation of Pb(II). Lead in the organic form of black tin has toxicity level of 1-100 ppm, a little bit higher than copper (Cu) and mercury (Hg) [2-3]. Development of techniques and innovations in treatment of Pb(II)-contained-waste has gained much attention with the main aim to minimize its concentration in the environment. The techniques include chemical precipitation, evaporation, cementation electrolysis, reverse osmosis, ion exchange [4], activated carbon adsorption [5] and coagulation [6]. Among the other methods, coagulation is known as the most effective method in minimizing heavy metal concentration in waste water [7-8].

Now, coagulation technique is directed to become biocoagulation as environmental (biodegradability) and economical aspects should be considered. Biocoagulation may become promising and potential technique in the Pb(II) waste water treatment due to the availability of various coagulations, for instance chitosan as by product from fisheries industry [9]. Chitosan has been employed as coagulant and adsorbent [10]. Chitin and chitosan are nontoxic and biodegradable [11-12].

Chitosan is a material produced via deacetylation of chitin using strong base. Chitin and chitosan are largely found at crustaceans, like shrimp and crab [6]. Chitosan is a polymer that can be obtained from the shells of seafood such as prawns, crabs, and lobsters. Chitosan has free amino groups, which can attract

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metal ions, and has been used as an adsorbent for the removal of metal ions from effluents [13]. Shrimp is the main export commodity that supports the income for the country. Shrimp shell contains protein (25-40%) and chitin (15-50%) [7]. Since the amount of waste from shrimp processing is quite high, further utilizations of the shrimp waste is required. An effort to overcome the waste problem is by converting it into valuable product such as chitin and chitosan. Chitosan is easily degraded. Besides, it can be effectively applied in the removal of organic contaminants (humic substances from surface waters, emulsified oils in food and petroleum industries, rubber particles, etc.) [1] and hazardous heavy metals from waste waters of galvanic, automotive, and microelectronic industries which produce large volumes of wastes containing Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cr^{3+} [14-15]. Gyananath et al. [4] stated that chitosan has high chemical reactivity and has the nature of polyelectrolyte cation, hence, it could be applied as ion exchange, chelating agent [3] and coagulant of Pb(II) in waste water. Chitosan has three reactive groups of primary (C-6) and secondary (C-3) hydroxyl groups on each repeating unit and the amino (C-2) group on each deacetylated unit. These reactive groups are readily subject to chemical modifications to alter mechanical and physical properties of chitosan [16].

By considering the potential and availability of chitosan, research on application of chitosan as coagulant in Pb(II) treatment was conducted with the main aim to support government to solve waste problems and to increase society's wealth. According to Lukum [17], chitosan from *Peneaus monodon* cultivated in Gorontalo has deacetylation degree of 80%. Such value was comparable with that of commercial chitosan. The produced chitosan was then applied to treat the Pb(II) on the waste water from Tolangohula sugar factory. In this research, effect of coagulant mass, pH to remove lead from liquid waste of Tolangohula sugar factory would be evaluated.

EXPERIMENTAL SECTION

Materials

Chitosan as absorber was extracted from shell *Peneaus monodon* with deacetylation degree of 80%, standard solution of lead (Pb(II)) p.a, hydrochloric acid (HCl) p.a, sodium hydroxide (NaOH) p.a, potassium iodide (KI) p.a, nitric acid (HNO_3) p.a and aquadest.

Instrumentation

Instruments used in this research were laboratory glasswares, oven, magnetic stirrer (thermoline), pH-meter (Janway), centrifuge, Atomic Absorption Spectrometer (AAS, Zeeman AA240Z).

Procedure

Preparation of liquid waste sample from Tolangohula sugar factory

Sampling technique was done according to SNI 6989.59:2008 about methods of liquid waste sampling. Since the sampling was specifically aimed to control waste water, liquid waste was taken on channel disposal before entering the receiving water. The sampling was focused on the reception tanks 5, which was the last tanks before the river. The sample was placed on dark bottle and preserved at pH 2 using concentrated HNO_3.

Qualitative analysis of the waste water from Tolangohula sugar factory

The qualitative analysis was conducted by preparing 3 test tubes filled with 5 mL of waste water sample for each. Then, solutions of HCl 0.5 M, NaOH 0.1 M and KI 0.5 M was added dropwise. The mixture was shaken and the resulted precipitate was also observed.

Coagulation and flocculation of Pb(II) using chitosan

The coagulation and flocculation procedures in this research were referred [4,18] with slight modification using *Jar-test* method.

In the study of effect of chitosan mass, 150 mL of waste water was contacted with chitosan with different mass (0, 2.5, 5, 7.7 and 10 g). The mixture was stirred at maximum speed for 1 min followed with stirring at medium speed for 30 min. The mixture was stand from 5 min and led to separate. The upper layer was taken and centrifuged for 15 min to give sediment and filtrate. The resulted filtrate was analyzed with AAS. The amount of removed Pb(II) was calculated from the difference between metal concentration of blank and after the coagulation process.

In the determination of the optimum coagulation pH, 300 mL of waste water and chitosan (optimum mass) were placed on Erlenmeyer. The pH was adjusted to be 2, 6, 7, 8, 9 and 10 using NaOH and HCl. The mixture was stirred at maximum speed for 1 min followed with stirring at medium speed for 30 min. The mixture was stand from 5 min and led to separate. The upper layer was taken and centrifuged for 15 min to give sediment and filtrate. The resulted filtrate was analyzed with AAS. The amount of removed Pb(II) was calculated from the difference between metal concentration of blank and after the coagulation process.

Table 1. Results of qualitative analysis of Pb(II) in liquid waste in Tolangohula sugar factory

No	Reagent	Reaction	Explanation
1.	HCl 0.5 M	$Pb(^{2+} + 2Cl^- \rightarrow PbCl_2\downarrow$ (White precipitation)	Positive(Pb(II))
2.	NaOH 0.1 M	$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2\downarrow$ (White precipitation)	Positive (Pb(II))
3.	KI 0.5 M	$Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow$ (Yellow precipitation)	Positive (Pb(II))

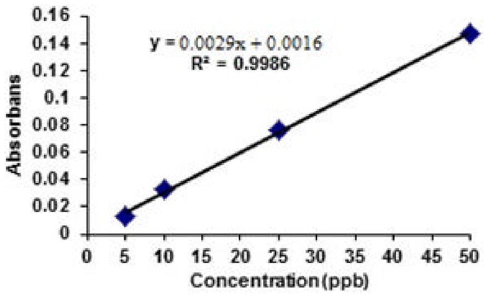
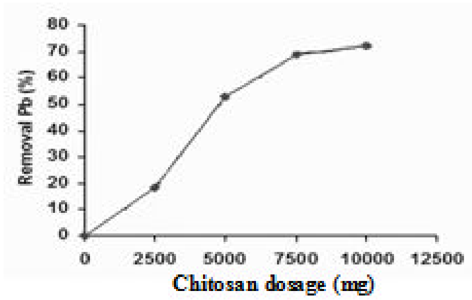


Fig 1. Calibration Curve of Pb(II)



Desc. Pb(II) concentration before coagulation was 30.79 µg/L
Pb(II) concentration after absorption (µg/L) = Pb(II) concentration before coagulation – Pb(II) concentration after coagulation

Fig 2. Removal Pb(II) percentage by varying the mass of chitosan (initial pH = 2)

Preparation of standard solution and calibration Curve

Solution of Pb(II) (100 ppb) was produced by diluting 10 mL of Pb(II) solution (1000 ppb) to 100 mL. Then, solutions of Pb(II) of 5, 10, 25 and 50 pPb(II) was prepared by dissolving 2.5, 5, 12.5 and 25 mL of Pb(II) 100 ppm in 50 mL of aquadest. Calibration curve was produced using standard solution of 0, 5, 10, 25 and 50 pPb(II) at wavelength of 283 nm. Standard absorbance Y as the function of standard concentration X could be written as equation of Y = aX + b.

Determination of Pb(II) concentration

The sample was analyzed using AAS using the same condition as the standard at wavelength of 283 nm to give the absorbance. The obtained absorbance was substituted to the linear equation to give the concentration of Pb(II) in the sample.

Data analysis

The ability of chitosan coagulation in coagulating metal Pb(II) was determined by entering data from sample measuring in regression equation of y = a + bx.

RESULT AND DISCUSSION

Qualitative Analysis of the Waste Water from Tolangohula Sugar Factory

The qualitative analysis of Pb(II) in waste water was conducted using reagent of HCl, NaOH and KI. According to Table 1, all the tests positively indicate that Pb(II) existed in the factory's waste water.

Preparation of Calibration Curve

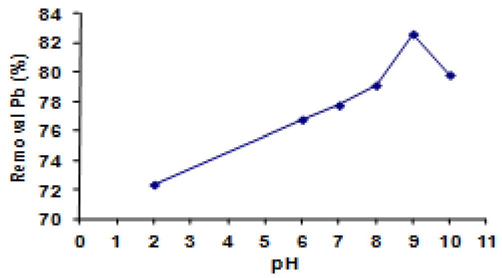
Analysis of Pb(II) in waste water using AAS was based on SNI 06-6989.8-2004. Calibration curve was required to determine the sample concentration. The analysis was conducted at the wavelength of 283 nm. Plot of absorbance Y and concentration X was presented gave calibration curve with equation of Y = 0.0029X + 0.0016 with coefficient correlation (r) = 0.99 (Fig. 1). The concentration of Pb(II) in the sample is 37.79 x 10^{-6} mg/g.

Determination of Percentage Pb(II) Removed from Waste Water of Tolangohula Sugar Factory: Effect of Coagulant Chitosan Mass

In the study of coagulant chitosan mass, waste water (pH = 2) was mixed with chitosan with various masses of 0, 2.5, 5, 7.5 and 10 g. The mixture was stirred at maximum speed for 1 min to homogenize the solution, followed with stirring at medium speed for 30 min to maximize the coagulation process (lump formation). The sample was precipitated for 15 min in forming flocs.

Chitosan could adsorb Pb(II) when the amine existed as uncharged group indicating that the mechanism occurred via chelate formation [18]. In this case, Pb(II) formed 5-membered-nitrogen and oxygen chitosan chelate ring [19].

To separate filtrate and sediment, each sample was centrifuged for 15 min. Then, the filtrate was analyzed using AAS method to determine Pb(II)



Desc. Pb(II) concentration before coagulation was 30.79 µg/L
Pb(II) concentration after absorption (µg/L) = Pb(II) concentration before coagulation – Pb(II) concentration after coagulation

Fig 3. Removal Pb(II) percentage by varying the pH of solution (chitosan dosage 10 g)

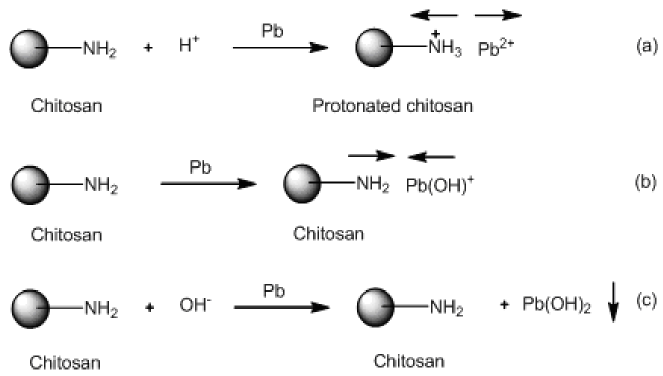


Fig 4. Interaction of chitosan and lead at (a) low; (b) medium and (c) high pH values

concentration.

Fig. 2 showed that the addition of chitosan could reduce the Pb(II) in waste water. In addition, the more chitosan mass, the higher the Pb(II) removal percentage. The Pb(II) removal increased and reached maximum (72%) when 10 g of chitosan applied. According to the results, it could be said that chitosan had ability to remove Pb(II) in liquid waste water in Tolangohula sugar factory.

Determination of Percentage of Pb(II) Removed from Waste Water of Tolangohula Sugar Factory: Effect of pH

To determine the optimum pH in the removal of Pb(II) in waste water using chitosan coagulant, as much as 10 g of chitosan was mixed with 150 mL of waste water. The pH was adjusted to be 2, 6, 7, 8, 9 and 10. The mixture was stirred, centrifuged and analyzed using AAS.

Fig. 3 showed that coagulation of Pb(II) using chitosan was dependant on pH [20]. The Pb(II) removal increased from pH 2 to 9 and reached maximum at pH 9 (83%). The removal percentage decreased at pH 10. These phenomena could be explained by evaluating two factors: the active sites of coagulant and speciation of Pb(II) in aqueous solution.

Kovacevic et al. [21] stated that at pH below 7, $Pb(II)^{2+}$ is the main ion in solution. On the other hand, the protonation of amine group of chitosan occurred and gave positively-charged amine salts. Therefore, there was repulsion between the metal ion and protonated coagulant. Besides, there was also dual competition of both hydronium ion (H^+) and lead (Pb(II)) to be adsorbed on the coagulant. In this case, adsorption of H^+ was predominated as its concentration is high in low pH value (Fig. 4.a).

At pH 6-9, $PbOH^+$ was dominant in the solution. With the increase of pH of solution, the degree of protonation of the coagulant active groups reduced gradually, thus, the amine of chitosan existed as free amine group. The amine group could use its electrons to interact with the lead ion via electrostatic interaction. Therefore, the absorption could increase from pH 6-9 (Fig. 4.b). At higher pH value, concentration of hydroxide (^-OH) ion increases. The decrease of Pb(II) removal at pH 10 was due to the formation of $Pb(OH)_2$, thus, decreased the electrostatic interaction (Fig. 4.c).

CONCLUSION

Chitosan obtained from *Peneaus monodon* could be applied as coagulant to treat Pb(II)-contained-waste water from Tolangohula sugar factory, Gorontalo. The optimum results were obtained using the mass of chitosan of 10 g at pH 9 for 100 mL sample containing 25.44×10^{-6} mg/g of Pb(II) removal.

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