

Chitosan Performance Of Shrimp Shells In The Biosorption Ion Metal Of Cadmium, Lead And Nickel Based On Variations pH Interaction

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Abstract—The widespread use of chitosan waste shrimp extract to reduce the toxicity of certain heavy metals can reduce the escalation of the potential threat of environmental pollution. First) shrimp shell processing is intensively done so it is not wasted freely into the environment, second) toxicity of heavy metals decreased significantly with the application of chitosan adsorption method to heavy metals conducted in wider society. Bioadsorption method of heavy metals of ions Cadmium, Lead and Nickel using chitosan begins with insulation chitosan shell chitosan. The isolated chitosan was characterized. The performance of chitosan adsorption the three types of heavy metal tests was determined by chitosan interaction of each metal at varying pH interactions (pH 2-8). Interaction media conditions: 100 mL medium volume, total chitosan used 1 g, contact time 60 min, the heavy metal concentration of 200 µg/g cadmium ion test, Lead ions and Nickel respectively 100 µg/g. Determination of absorbance using Atomic Absorption Spectrophotometer. The measured value of the adsorbent is converted to the maximum chitosan adsorption concentration value. The adsorption capacity of metallic chitosan complex, maximum was achieved for metal Cd²⁺ at pH 2 of 198.2051 µg/g (99.05 %), metal Pb²⁺ at pH 4 of 59.3341 µg/g (59.33 %) and metals Ni²⁺ at pH 7 of 45.1334 µg/g (45.13 %). This result indicates that pH value of interaction media has an effect on chitosan adsorption to heavy metal test with Cd²⁺ >> Pb²⁺ > Ni²⁺ sequence

Keywords— *shrimp shell, chitosan, adsorption, heavy metal, pH*

I. INTRODUCTION

Indonesia is one of the countries producing frozen shrimp. Shrimp processing centre is spreading in many areas in Indonesia, including Makassar. Shrimp processing

business produces waste material especially shrimp shell, It reaches (30 - 70) %, [1]. Shrimp waste volume has the potential to have a negative impact on the environment. Chitin content in shrimp shells reaches (15 - 20) %, [2] protein (25-40)%, [3, 4] and calcium carbonate (45 - 50) %, [5]. Chitin is a polysaccharide group, a linear chain polymer and high molecular weight [β - (1-4) -2-acetamide-2-deoxy-D-glucose], can be converted into chitosan through the stages deproteinize (addition of aqueous NaOH), stage of demineralization (addition of low concentration HCl) and deacetylation stage (strong base reaction NaOH 50 %), [6]. The deacetylation reaction of chitin by removing the acetyl group (CH₃CONH-) produces chitosan polymer [β - (1-4) - 2-amine-2-deoxy-D-glucose], molecular formula (C₆H₁₁NO₄)_n, polycationic, high and reactive solubility, [2,7,8,9]. Chitosan is a yellowish-white amorphous solid polymer, potentially used as a heavy metal adsorbent by the mechanism of free electron-donor pair (Lewis bases) in hydroxy group (-OH) and amine (-NH₂) to form pseudo-bonds with heavy metal cations resulting in a chitosan-metal weight of complex, [7,10].

The heavy metal form of the substance is classified as dangerous and toxic because it is toxic to the environment of water, soil and air. Exposure to heavy metal ions to humans poses serious health problems, [11]. The heavy metal ions, for example, Chromium (Cr). Cobalt (Ni), Copper (Cu), Zinc (Zn), Manganese (Mn), Silver (Ag), Cadmium (Cd), Lead (Pb), Mercury (Hg), Arsenic (Ar), Selenium (Se) and other heavy metals, [12, 13, 14]. Based on the potential sources of contamination, exposure and risks to health, the three types of heavy metals form Cd²⁺, Pb²⁺ and Ni²⁺ are unstable free radical ions, so they should receive special attention handling, aimed at reducing

and reducing their toxicity to the environment, [13, 15, 16, 17].

The adsorption of chitosan on some heavy metal ions is unstable, becoming one of the alternatives to reduce the potential health risks of exposure to heavy metal toxic ions and is expected to be the most widely performed option. The use of chitosan modification or chitosan of activation for heavy metal ion absorption can overcome two problems at once, namely the need chitin-chitosan increased, resulting in the processing of shrimp shells become chitosan continuous so as not to form potential waste pollute the environment, as well as potential heavy metal contamination in the environment, minimized, [18, 19, 20, 21, 22].

II. MATERIALS AND METHODS

1. Materials and equipment

Materials used: White shrimp shell (*Penaeus merguensis*), HCl p.a, NaOH p.a, CH₃COOH p.a, NiSO₄.6H₂O p.a, Cd(NO₃)₂.4.H₂O pa, Pb(NO₃)₂ pa, AgNO₃ pa, Ninhidride, PP Indicator, glacial acetic acid, whatman paper no. 42, Aquades. Equipment: digital scales, stop watch, 1 set of crusher, Magnetic stirrer 79-1, Oven memmert UNB-400, Desiccator, Universal pH, Thermometer, centrifugation tool, 100 mesh sieve, Glassware, Volume Pipette, Atomic Absorption Spectrophotometer (AAS) merk Buck Scientific.

2. Preparing the chitosan

Separating the chitosan from the shell is done by several steps, they are: (1) Adsorbent preparation steps: washed the shrimp shells, dried, mashed, sieved in 100 mesh sized; (2) Demineralisation step: add HCl 1,5 M to the dried shell with the comparison 1:15 (b/v), heated it in 70 °C for 3 hours, stirred centrifugated it for about 15 minutes spin of 200 rpm, it will resulted as supernatan, then washed it with aquades up to no more of HCl substance on it, the last filtrate taken by washed it with AgNO₃ so there will be no more precipitation.

3. Chitosan Preparation

The isolation of chitosan from shrimp shell is done in several stages, namely; (1) preparation phase of adsorbent: shrimp shell washed, dried, mashed, sieved size 100 mesh; (2) Demineralization stage: dry rendamen plus HCl solution 1.5 M, ratio 1:15 (w/v), heated temperature 70 °C for 3 hours, stirred, centrifuged for 15 minutes 200 rpm rotation, supernatant dipole, then washed with aquades until free HCl, the final filtrate obtained was washed with AgNO₃ until there was no precipitate; (3) Deproteinization stage: convert protein bound to shrimp shell to salt of sodium proteinate with addition of 3.5 % NaOH ratio 1:10 (w/v), heated temperature (40 to 50) °C for 4 hours while stirring speed 50 rpm, filtered to obtain residues (chitin) and filtrate formed in the test with pp indicator until no red brick changes occur. Chitin is washed with aquades, then dried in

an 80 °C oven for 24 hours, disentangled in a desiccator. The obtained rendaments were measured; (4) Deacetylation stage: deproteination result is continued addition of NaOH 60 %, 1:20 (w/v). Stirred 50 rpm and heated, temperature 45 °C, for 4 hours, centrifuged 15 minutes, 200 rpm, supernatant was then neutralized with aquades, dried in 80 °C oven for 24 hours, chitosan was obtained. The obtained chitosan was characterized by parameters: organoleptic test (odor test, texture, color), rendamine, water content, solubility and test with ninhydrin.

4. Determination of concentrations of Cd, Pb and Ni adsorbate

- The standard solution of each of the metal ions Cd, Pb and Ni was made 1,000 ppm, diluted gradually to obtain Cd 200 µg/g ion ions and Pb metal ions as well as Ni metal ions of 100 µg/g each. The adsorption parameter based on 7 variations of pH interaction, ie pH 2 to 8, chitosan interaction medium to the three types of test metal ions in constant condition, namely: 100 mL metal ion solution volume, homogenization using 15 min magnetic stirrer contact time 60 min, and the amount of chitosan used respectively ± 1.0 g each treatment.
- Interaction procedure (Cd²⁺ metal interaction of chitosan): Prepared 7 of volume 100 mL erlenmeyer labels labeled pH 2 to 8, filled with Cd²⁺ solution, 1.03 g of chitosan each added, homogenized using 15 min magnetic stirrer, silenced for 60 minutes, filtered with whatman no. 42, 50 mL filtrate was taken in 50 mL erlenmeyer, pH was conditioned at 2 to 8 using HNO₃/NaOH above magnetic stirrer, Cd²⁺ absorbance value was measured with AAS $\lambda_{\max} = 228.80$ nm. The same procedure was performed for the determination of Pb²⁺ $\lambda_{\max} = 217,00$ nm and Ni²⁺ $\lambda_{\max} = 232,10$ nm. Determination of adsorption power and chitosan adsorption concentration on 3 kinds of metal ions based on uptake was calculated using linear equation.

III. RESULTS AND DISCUSSION

The results of shrimp chitosan isolation are presented in Table 1.

Table 1. Rendemen of Chitosan

Num	Measurement	Value
1	The initial weight of the shrimp shell	300.03 g
2	Weight after demineralization	138.02 g
3	Weight after deproteination	96.73
4	Rendemen chitin (%) / weight (g)	35.86/107.58
5	Chitin weights are converted to chitosan (g)	107.01 g
6	Rendements of chitosan (%) / weight (g)	65.17/ 69.74

The data Table 1, shows that chitosan content obtained is high in 65.17 %, equivalent to 23. 23 g of chitosan per 100 g shrimp shell (*Penaeus merguensis*), [1]. The treatment of chitosan isolation was carried out with the demineralization-deproteination-deacetylati-on stage,[2,7] whereas some previous studies carried out chitin insulation with the working order of deproteination-demineralization-deacetylati-on, and other modifications, [10,22,24], was performed to avoid the formation of a strong protective function by the skin due to the mineral calcium carbonate present in it. The first stage of chitosan isolation is demineralized so that the chitin content obtained is higher and the quality is better (the color is whiter and odorless), [3,8].

The results of chitosan characterization are presented in Table 2, the following:

Table 2. Characterization of shrimp shell chitosan

Parameters	Value of chitosan obtained	International standard chitosan value.
Water content	1.58 %	< 10 %
Solubility	Late	Late
Texture	Powder	Powder
Color	Pale white	White-pale yellow
Smell	No smell	No smell
Test ninhydrin	positive	-

Table 2 presents that the chitosan content obtained is in line of the international standards, [9,22]. The solubility of chitosan in 2 % glacial acetic acid solution is one of chitosan quality assessment parameters isolated from shrimp shell, [1,20,23]. The determinants of chitosan as a metal adsorbent are seen in the negative charge (surface group), ie (-OH) and (-NH₂). The number of amine groups in chitosan is the success of the isolation method. The -NH₂ group on chitosan is seen through the reaction of the purple ninhydrin solution indicating a reduction reaction at pH 6 to 8 forming a bonding compound between ninhydrin and hydrinadantin, [2,9].

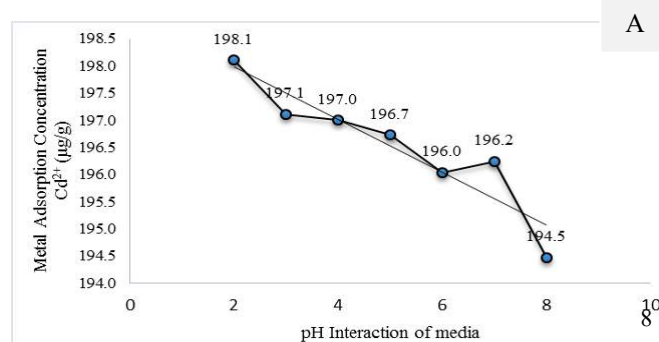
Table 3. Concentrations of Ion Metals Cd, Pb, and Ni Adsorbed

pH of metal chitosan -metal interaction	The average metal ion concentration on is not adsorbed	The average concentration of adsorbed metal ions (µg / g)	% Average metal ion adsorption	Decrease in adsorption value based on increase in pH (%)
<i>Metal interaction Cd²⁺-chitosan [200 (µg/g)/g]</i>				
2	1.8947	198.1053	99.0527	-
3	2.8897	197.1103	98.5552	-0.4975
4	3.0045	196.9955	98.4978	-0.5549
5	3.2777	196.7223	98.3612	-0.6915
6	3.9666	196.0334	98.0167	-1.03595
7	3.7630	196.2370	98.1185	-0.93415
8	5.5338	194.4662	97.2331	-1.81955
<i>Metal interaction Pb²⁺-chitosan [100 (µg/g)/g]</i>				
2	47.6548	52.3452	52.3452	-
3	43.7659	56.2341	56.2341	3.8889
4	40.6659	59.3341	59.3341	6.9889
5	46.9236	53.0764	53.0764	0.7312
6	46.7153	53.2847	53.2847	0.9395
7	47.6784	52.3216	52.3216	-0.0236

8	53.1207	46.8793	46.8793	-5.4659
<i>Metal interaction Ni²⁺-chitosan [100 (µg/g)/g]</i>				
2	76.5146	23.4854	23.4854	-
3	70.4706	29.5294	29.5294	6.044
4	65.6612	34.3388	34.3388	10.8534
5	63.2068	36.7932	36.7932	13.3078
6	60.8666	39.1334	39.1334	15.648
7	54.8666	45.1334	45.1334	21.648
8	72.2472	27.7528	27.7528	4.2674

The adsorption capacity of chitosan to metal ions Cd, Pb and Ni as shown in Table 3 and Figure 1, is done based on pH variation of interaction medium giving an idea that the pH of the interaction medium influences chitosan ability in absorbing certain metal type. The adsorption capacity of chitosan to heavy metal type, determined by the existence of active group form chitosan structure, that is: -OH and -NH₂. Both of these are ligands. The strength of the -NH₂ligand is stronger than -OH. The performance of chitosan adsorption to the metal ions determined by the active side of chitosan will be decreased equivalent to the amount of adsorbent of metal ions absorbed, so that chitosan is saturated, [1, 20, 24].

The mechanism of interaction is the reaction of the formation of complex compounds between chitosan and metal ions. The application of chitosan with the highest Cd²⁺ metal at pH 2, continues to decrease as the pH increases in the interaction medium to 7 to the highest chitosan impairment performance at pH 8 (Figure 1, a), but the chitosan adsorption to Cd²⁺ metal is much higher than that of Pb²⁺ and Ni²⁺, occurs because the complexity of Cd²⁺ metal chitosan can occur in two complex forming mechanisms, namely: first, the internal chitosan complexes of glucopyranose monomers use two pairs of free electron pairs each pair of free electron -OH groups and a pair of free electron -NH₂ groups in one the glucopyranose molecule forms a false bond with Cd²⁺, this complex compound forms a polymer chain called polymer monolayer complex,[13, 19]. The second, Adsorption of Cd²⁺ metal by chitosan to form chitosan-metal complex also can occur combination of α-cluster bonding of group in first layer glucopiranic monomer to form cadmium bridge with subsequent group -NH₂ glucopyranose layer and reverse pseudo-bonding of first group -NH₂ glocopiranososa layer with -OH group the glucopyranous molecule of the underlying layer, this state is called the polymer doublelayer complex, [10,12]. The ability of chitosan adsorption of Cd²⁺ metal ions in 2 complex forming mechanisms causes the concentration of cadmium metal to be absorbed by the highest chitosan active groups compared to lead and nickel metals, [22,25].



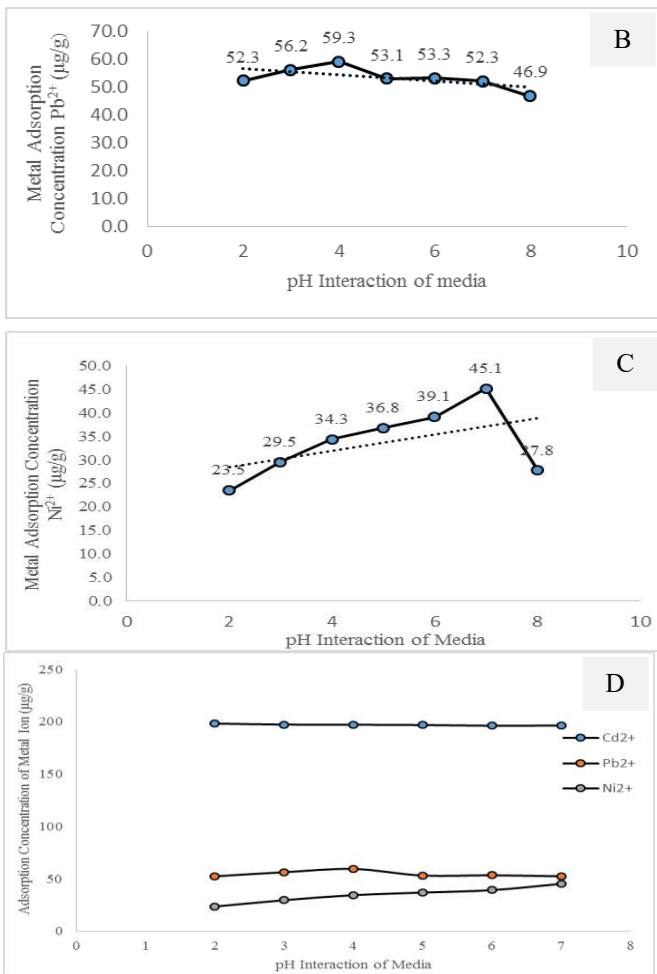


Figure 1. Performance of Chitosan shrimp-shell of Adsorption on Metal Ion ($\mu\text{g/g}$) Based on Variation of pH Media Interaction. A) Metal Cd^{2+} ; B) Metal Pb^{2+} ; C) Ni^{2+} , D) Combined Metal Cd^{2+} .

The formation of Chitosan-Pb and Chitosan-Ni complexes formed only 1 reaction mechanism ie metal adsorption of $\text{Pb}^{2+}/\text{Ni}^{2+}$ by chitosan formed complex of chitosan-metal occurs in the combination of group bonds in first layer glucopyranose monomers forming Lead/Nickel bridges with cluster $-\text{NH}_2$ glucopyranose the subsequent layer and vice versa of the first-layer $-\text{NH}_2$ glucopyranous group binding with the $-\text{OH}$ group of glucopyranous subcutaneous molecules below, so that the concentration of the metal lead/Nickel absorbed by chitosan is limited due to faster saturation in chitosan active part (Table 3) and (Fig. 1. B, C), [7, 15]. The maximum adsorption of chitosan against metal Pb^{2+} formed Chitosan-lead complexes occurred at pH 4 interaction media conditions, while the chitosan-nickel complex, maximum at pH 7, (Table 3).

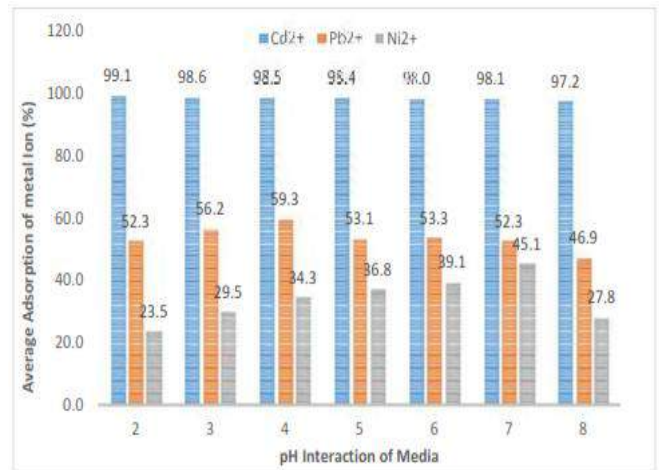


Figure 2. Average Power Adsorption Chitosan Shrimp Shells Against Metal Cd^{2+} , Pb^{2+} , Ni^{2+} (%) based on pH variation Media Interaction

The average adsorption capacity of chitosan to metal Cadmium, Lead and Nickel (Figure 2) the largest consecutive Cadmium \gg Lead $>$ Nickel, (Figure 1. D). The maximum absorption power of chitosan-Cadmium occurs in conditions of pH 2 media interaction, chitosan-Lead at pH 4, whereas the chitosan-Nickel adsorption occurred at pH 7. The difference in the adsorption capacity of chitosan for the metal and pH difference interactive media to achieve maximum adsorption due to several factors: first) the type and density of metal that interacts with chitosan, second) metal forming capabilities variation reaction mechanism of chitosan-metal complex formation, third) the ability of chitosan to release a proton (H^+) in the group $-\text{OH}$ and $-\text{NH}_2$ in a certain pH value of media interaction. Adsorption capacity of chitosan against specific types of metal so that the pH value of a medium of interaction varied to achieve optimum adsorption, [19,20].

IV. CONCLUSION

Result of investigation of chitosan adsorption to metal ion test, concluded: *The first*, Chitosan of shrimp shell waste extract can be used as biomaterial absorption of heavy metal of ions Cadmium (Cd), Lead (Pb) and Nickel (Ni); *second*, range of optimum pH of shrimp shell chitosan adsorption against heavy metal ions Cadmium (Cd^{2+}) at pH 2 to 5, Lead (Pb^{2+}) at pH 3 to 6 and Nickel (Ni^{2+}) at pH 5 to 7; *third*, the maximum adsorption value of chitosan to heavy metal Cd^{2+} was 198,2051 $\mu\text{g/g}$ (99.05 %) achieved at pH 2, metal Pb^{2+} was 59.3341 $\mu\text{g/g}$ (59.33 %) achieved at pH4 and metal Ni^{2+} was 45.1334 $\mu\text{g/g}$ (45.13 %) was achieved at pH 7; *fourth*, the order of adsorption power of shell shrimp of chitosan to the heavy metal test is $\text{Cd}^{2+} \gg \text{Pb}^{2+} > \text{Ni}^{2+}$.

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