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Separation of Heavy Metals Copper (Cu) and Nickel (Ni) from Industrial Wastewater by Adsorption Using Chitosan Shrimp Shell

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Abstract

Shrimp shell contains chittin that can be processed become chitosan. Chitosan can be used as bioadsorbent to treat heavy metals content in wastewater. The purposes of this research are to find deacethylation degree of chitosan from shrimp shell, the constant value of adsorption affinity (k) and adsorption efficiency for various variation mass and size of chitosan, heavy metal concentration (solute) in wastewater and to compare adsorption efficiency between syntetic solution and industrial wastewater. The size variation of the chitosan are 20 mesh and 40 mesh. The type of adsorption used is batch until 4 hours with 5 rpm as agitation rate. Deasethylization degree for chitosan 20 mesh and 40 mesh are resulted as 75,61% and 77,71 %. More amount of chitosan used and the smaller size of chitosan make the adsorption efficiency higher as 92,52%. A synthetic solution and PT SIER industrial wastewater are types of wastewater used. PT SIER wastewater contains other metals that can hamper the adsorption of desired metals. Ni is easier to adsorp with 92,52% efficiency than Cu which has efficiency of 88,52%, because atomic radius of Ni is smaller than Cu. Adsorption affinity constant is influenced by size of the chitosan. The smaller size of chitosan make adsorption affinity constant higher than the bigger size (which is 0,13).

Keywords: adsorption, shrimp shell, chitosan, heavy metal, nickel, copper

1. Introduction

The development of industry, agriculture, and domestic activities in Indonesia led to increase amount of waste water that can pollute the waters. Waste water from industrial and mining, such as iron and steel industry, metal plating industry, mining industry, packaging industry, and the textile industry are a major source of heavy metal pollutants. This waste causes serious pollution to the environment if the content of heavy metals exceeds the threshold content and have toxic properties which are very dangerous and cause serious diseases to humans if it accumulates in the human body.

Several methods have been developed to reduce levels of heavy metals from industrial waste water, for example the method of precipitation, evaporation, electrochemical and adsorption by conventional adsorbents. Adsorption process is widely used in industry because it has more economical and also does not cause toxic side effects and is able to eliminate the organic materials. Conventional adsorbent has good adsorption capability but require operating costs and relatively expensive regeneration. Therefore we need an alternative adsorbent derived from nature, because in addition to having good adsorption capability, the adsorbent is also more economical. One of the adsorbent which has a good prospect is a biological material.

There are many natural resources in the field of fisheries in Indonesia which is very abundant. One of the potential of these resources is shrimp. Indonesian shrimp are usually stored after the disposal of the head, skin and tail. The results of this waste can pollute the environment surrounding the waste site. One alternative could be use the waste into chitosan product that is a polysaccharide derived from chitin. Chitosan as bioadsorben can be used to adsorb heavy metal ions which contained in the waste water industry. Chitosan from waste of shrimp shell has a higher adsorption capacity compared to other alternative adsorbents, which is 5.93 mg / g for the metals Cd, 815 mg / g for Hg, 222 mg / g for Cu, 164 mg / g for Ni, and 75 mg / g for Zn.

In this research, copper (Cu) and nickel (Ni) will be adsorped. Selection of Cu and Ni metal because the metal is used in the metal plating industry, household appliance industry, packaging industry, and the electronics company that can pollute the environment if the concentration exceeds the threshold. Cu metal used for various electrical and household appliance, electronic components, and so on. Ni metal is used on a large scale for the manufacture of stainless steel and other alloys that are corrosion resistant.

2. Method

Adsorption is a process of adsorption by certain solids of certain substances that occur on the surface of solids due to the attractive force of atoms or molecules on solid surfaces without soak into. To know the characteristics that occur in the adsorption process can be illustrated by Figure 1, the solid porous (pores) that suck (adsorp) and release (desorp) a fluid called the adsorbent. Fluid molecules smoked but did not accumulate / attached to the surface of the adsorbent is called adsorptive, while the accumulated / attached called adsorbate.

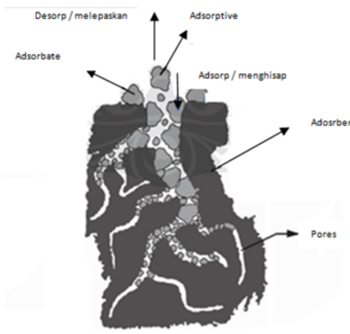


Figure 1. Adsorption Nomenclature (Wahyu, 2008)

2.1 Industrial Waste Water

Industrial waste water contain pollutants that are toxic and dangerous as hazardous matter. This material is formulated as an ingredient in a number of relatively small but have the potential to pollute and destroy the lives and resources. In this research, industrial waste water is obtained from PT. SIER. Waste water PT. SIER contain some heavy metals in low concentrations. As the concentration of heavy metals contained in waste water PT. SIER can be seen in Table 1.

Table 1. Concentration of heavy metals in waste water PT. SIER

Parameter	Concentration (ppm)
Iron (Fe)	0,185
Copper (Cu)	0,62
Cadmium (Cd)	0,13
Nickel (Ni)	0,91

(Source: Daily Report of Water Laboratory in PT. SIER).

2.2 Heavy Metals

Heavy metals still belonged to the metal with the same criteria as the criteria other metals. The difference lies in the effect of produced when heavy metals and or bonded into the body of living organisms. In contrast to common metals, heavy metals usually cause special effects in living organisms. It can be said that all the heavy metals can be toxic to living bodies (Palar, 2004)

2.2.1 Copper

Copper is one of the heavy metals are dangerous because these elements can disrupt the respiratory tract. But in a very small amount of a metal or mineral that is essential for the body. At the excess amount, it will be changed into substances that toxic to the human body.

2.2.2 Nickel

Nickel is a metallic chemical element in the periodic table has the symbol Ni and atomic number 28. Nickel has stainless nature. Nickel in small amounts is needed by the body, but it can be harmful to human health in high amounts. High concentrations of nickel in sandy soils can damage crops and on the surface can reduce the levels of algae growth. Further alleged that the nickel is also able to inhibit the growth of microorganisms. Nickel toxicity on aquatic life depends on the species, pH, hardness and other environmental factors.

2.3 Biosorption

Biosorption is defined as the use of natural materials to bind heavy metals (Cossich et al., 2003).

The mechanism of metal ion occurs in biomaterial related to displacement of metal ions through the layer or wall surface. Phase displacement occurred as follow (Guibal et al., 1992):

a. Transfer of metal ions from the solution to the existing barrier films around the cell wall
b. Transfer of metal ions from the cell surface to the barrier films
c. Transfer of metal ions into the cell active biomaterial
d. Adsorption phase consisting of bond and sedimentation in the membrane of biomaterials.

2.4 Chitosan

Chitosan is obtained through deacetylation chitin processes. This polymer can be isolated from the skin of shrimp, crab skin, lobster, clams and even mushrooms (fungi). Chitosan has three types of functional groups, that are amino acid, primary and secondary hydroxyl. Quality parameter is the deacetylation degree of chitosan, water, ash and protein.

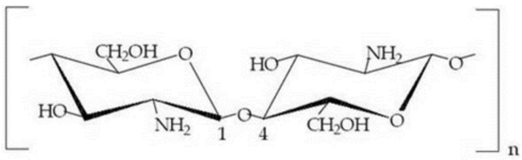


Figure 2. Structure of Chitosan

Table 2. Quality Parameters of Chitosan

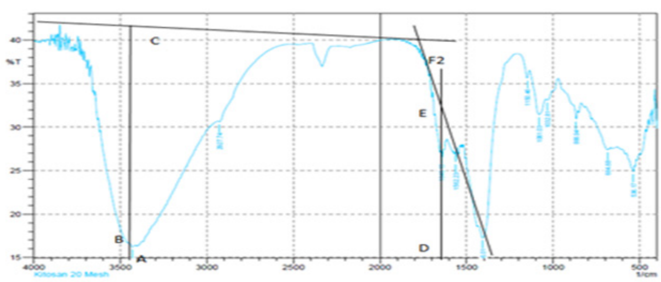
Parameter	Charateristic
Particle size	Flakes to powder
Water content (%)	≤ 10 %
Ash content (%)	≤ 2 %
Color of solution	Colorless
N-deacetylation (%)	≥ 70 %
Viscosity level (cps)	
- Low	< 200
- Medium	200 – 799
- High	800 – 2000
- Very high	< 2000

(Source: Protan in Manullang Laboratory, 1997).

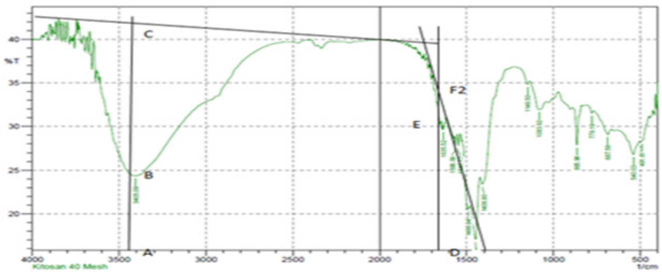
3. Results

Charateristics of Chitosan

Chemical characterization of chitosan can be analyzed by the spectra Infra Red (IR) to determine the functional groups of analyzed products, so that it can be concluded that the compound is expected chitosan. From figure 3a and figure 3b show that N-H adsorption is on wavelength 3450 cm^{-1} and adsorption for C=O is on wavelength 1655 cm^{-1}.



(a)



(b)

Figure 3. FTIR Spectrophotometry Analysis Curve of Chitosan (a) 20 Mesh and (b) 40 Mesh

% DD was determined by base line b method proposed by Baxter et al.

From the graph above, we obtained:

AB = 16,8

AC = 41,7

DF_2 = 32,5

DE = 26,8

A_{3450} is absorbance of wavenumbers 3450 cm^{-1} which shows adsorption of N-H and could be use as an intern standarization. A_{3450} can be calculated by using the formula:

A_{3450}= Log (AC/AB)

= Log (41,7/16,8)

= 0,394

A_{1655} is absorbance in wavenumbers 1655 cm-1 which shows adsorption of C=O. A_{1655} can be calculated by using the formula:

A_{1655}= Log (DF_2/DE)

= Log (32,5/26,8)

= 0,0837

From base line b method, we use equation:

$$\% \text{ DD} = 100 - \left[\left(\frac{A_{1655}}{A_{3450}}\right) x\ 115\right]$$

$$\% \text{ DD} = 100 - \left[\left(\frac{0{,}0837}{0{,}394}\right) x\ 115\right]$$

% DD = 100 – 32,878

% DD = 75,607 %

Table 3. Analysis Results for Deacetylation Degree

Chitosan Size (mesh)	%DD
20	75,607
40	77,712

The next step is the physics characterization which includes the determination of moisture content, ash, protein, and minerals, which compared with raw material (shrimp shells). From table 4, it can be seen that at this stage of demineralization and deproteinasi, mineral content and protein contained in the shrimp shells that can be eliminated or reduced. The presence of mineral and protein content of the chitosan pore can reduce the adsorption capacity of chitosan against heavy metals in synthetic solutions and wastewater.

Table 4. Water, Ash, Protein, and Mineral Content of Chitosan

Content (%)	Chitosan	Shrimp Shell Powder
Water	0,28%	12,35%
Ash	0,049%	17,13%
Protein	11,31%	47,18%
Mineral	Not detected	9,17%

4. Discussion

4.1 Effect of Agitation Time Against Decrease Metals Concentration

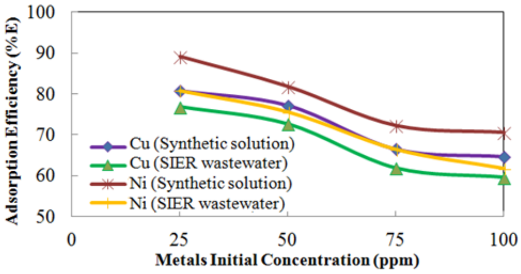


Figure 4. Effect of Agitation Time Against Decrease Metals Concentration Curve Use 1 gram Chitosan 20 mesh with Initial Concentration 25 ppm

From figure 4, it can be seen that the adsorption process of Cu and Ni with a agitation speed of 5 rpm showed a decrease in metal concentrations were relatively constant after 1 hour. This is because until 1 hour, chitosan is still active and has not been saturated by Cu and Ni. But, after 1 hour chitosan has been saturated and reduced its ability to bind metals.

4.2 Effect of Metal Type and Wastewater Type Against Adsorption Efficiency

From the analysis using AAS can be seen that metal type of Ni can adsorp easier than (Figure 5). This is because Ni atomic radius is 1.15 Å and 1.17 Å for Cu. Greater adsorption ability of chitosan on the metal atom is on smaller radius. Because the larger atomic radius has smaller ionization energy, so it gets easier to release electrons. If an element is easy to remove an electron, then the strength of the metallic bond get stronger. Cu atomic radius is larger than Ni, so the metallic bond is stronger and more difficult to adsorp than Ni.

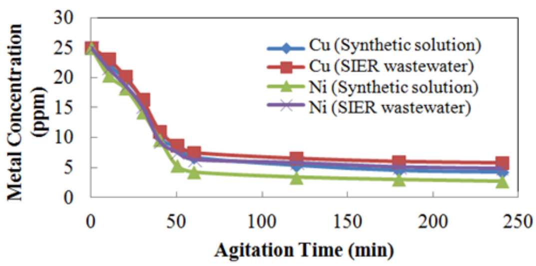


Figure 5. Effect of Metal Type and Wastewater Type Against Adsorption Efficiency Curve for Initial Concentration 25 ppm

From Figure 5 also shown that adsorption efficiency of chitosan for both Cu and Ni in SIER wastewater is smaller than synthetic solution. This is because the synthetic solution only contain Cu or Ni (one of them). In other hand, SIER wastewater contains other metals, such as cadmium (Cd) and iron (Fe) in which the metal is also adsorbed by chitosan, so capacity of chitosan to adsorp the desired metal will be decrease.

4.3 Effect of Initial Metal Concentration Against Adsorption Efficiency

Initial concentration variation of the metal in this study were 25, 50, 75, and 100 ppm. From Figure 3 it can be seen that by using 1 gram of chitosan 20 mesh, an increase in the initial concentration of metal in solution or SIER wastewater cause adsorption efficiency would be decreased. This happens because the chitosan surface will become saturated fast. This condition also occurs in variations in the weight and size of other chitosan. If the chitosan surface (adsorbent) is saturated or nearly saturated with adsorbate, it can happen two ways:

a) Adsorption layer formed on the second and so on that have been bound adsorbate on the surface. This phenomenon is called the multilayer adsorption.

b) Not formed a second layer and so on that are not adsorbed adsorbate will diffuse out and back into the flow of the pore fluid.

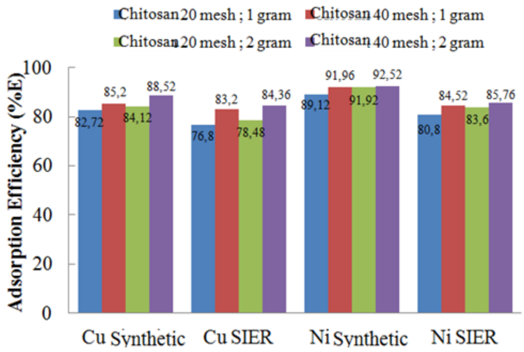


Figure 6. Effect of Initial Metal Concentration Curve by Using 1 gram Chitosan 20 mesh

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Appendiks A

Analysis Result to Determine Water, Ash, Protein, and Mineral Content of Chitosan

A.1 Water Content

Water Content (%) = (W2-W1)/W2 x 100%

where: W1= the weight of cup + chitosan after oven

W2= the weight of cup + the first of chitosan before oven

Water content of chitosan 20 mesh

W1 = 26,039 gram

W2 = 26,112 gram

Water content = (26,112 gram - 26,039 gram)/(26,112 gram) x 100% = 0,280 %

Water content of chitosan 40 mesh

W1 = 33,261 gram

W2 = 33,354 gram

Water content = (33,354 gram – 33,261 gram)/(33,354 gram) x 100% = 0,279 %

A.2 Ash Content

Ash Content (%) = (W2-W1)/W2 x 100%

Where: W1= the weight of cup + chitosan after furnace

W2= the weight of cup + the first of chitosan before furnace

Ash content of chitosan 20 mesh

W1 = 28,433 gram

W2 = 28,447 gram

Ash content = (28,447 gram – 28,433 gram)/28,447 x 100% = 0,049 %

Ash content of chitosan 40 mesh

W1 = 30,651 gram

W2 = 30,674 gram

Ash content = (30,674 gram – 30,651 gram)/(30,674 gram) x 100% = 0,075 %

A.3 Protein Content

To measure protein content of chitosan, Kjedahl Method are used. Samples were taken before and after the deproteination process.

A.4 Mineral Content

Atomic Adsorption Spectroscopy (AAS) is used to measure mineral content of chitosan. Samples were taken before and after the demineralization process.