# Utilization of Shrimp Shells as Biosorbent to Remove Heavy Metal Cu and Zn in Aquatic Samples

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***Abstract*****—** Indonesia is an archipelago country that has one of the longest coastal-line in the world. Despite its huge potential of Indonesian marine resources, the usage of marine resources to improve Indonesian people welfare is still low. In this study, utilization of shrimp-shell waste as potential biopolymer to increase its selling value that finally improves Indonesian fisherman welfare. Chitosan, a biopolymer prepared through the deacetylation of chitin, found in the exoskeleton of crustaceans (e.g. shrimp) is the most abundant amino polysaccharide in nature. Its chelating properties are attributed to the amino and hydroxyl groups that can act as chelation sites for different targets such as metals. We have synthesized and tested the ability of chitosan as a chelating resin for reduction of heavy metals concentration in aquatic samples. Scanning electron microscopy (SEM) was used to characterize the morphology of the chitosan surface. Fourier transform infrared (FTIR) characterization showed wavenumber 3447,64 $cm^{-1}$ and 1654,98 $cm^{-1}$ shows a ribbon for -OH and -NH groups on chitosan. Optimum adsorption conditions were studied for Cu (II) and Zn (II). The interest metals were analyzed using spectrophotometry method. We found that chitosan adsorption behaviour followed Langmuir isotherm.

***Keywords*****—** Chitosan, Chelating Resin, Heavy Metal, Indonesian Marine Resources.

## I. Introduction

THE presence of heavy metals in the environment has been of great interest due to their increased discharge, toxic nature and other adverse effects on receiving waters. Waste water from mining operations, metal-plating facilities, power generation facilities, corrosion, electronic device manufacturing units and tanneries often contain considerable amount of toxic heavy metals such as chromium, cadmium, lead, mercury, nickel and copper above local discharge limits. The toxicity of heavy metals might be caused by mechanisms that include blocking essential functional groups of biomolecules and disrupting the integrity of biomembranes. Divalent metal ions such as lead, copper, cadmium, mercury and nickel can cause severe health problems in animals and human beings related to their ability in bonding to proteins, nucleic acids and small metabolites in living organisms. This causes either alteration or loss of biological function and may disturb the homeostatic control of essential metals. The removal of toxic heavy metal ions from industrial effluents, water supplies and mine waters has received much attention in recent years. Various methods are available for such processes, including chemical precipitation, filtration, electrochemical treatment, ion exchange, liquid–liquid extraction, resins, sorption, cementation, and electrodialysis. Each method has been found to be limited by cost, complexity, and efficiency as well as by secondary waste. Among these methods sorption is one of the most effective and simplest approaches to separation processes for a wide variety of applications. It is now recognized as an effective and economic method for the removal of pollutants from wastewaters (Khan *et al*, 2011).

Various natural and synthetic polymeric materials have been synthesized or chemically modified for the removal of heavy metal ions from aqueous solutions. Synthetic polymers such as ion exchange resins and chelating resins have been widely used as effective sorbents to collect radioactive nuclides, toxic metals, precious metals and base metals from aqueous solutions. Naturally occurring biopolymers have also been shown to exhibit excellent sorption abilities for multivalent metal ions. Natural materials such as chitosan, zeolites, clay, coal, and some microbial biomass products are classified as low-cost sorbents due to their low initial cost and local availability. Indonesia is a maritime country with abundant chitin resources. Naturally occurring biopolymers are competing with the conventional technologies and other similar materials of biological origins that have been intensively used as sorbents for heavy metal ion removal from water and industrial effluents. Biopolymers are industrially attractive because they possess a capability of lowering transition metal ion concentrations to parts per billion. The group of such biopolymers includes cellulose, chitin, alginate, carrageens, lignins, some proteins and pectins (Yang *et al*, 2011).

Chitin is the second most abundant naturally occurring biopolymer. The largest sources are the exoskeletons of arthropods, especially crabs (Malacostraca) and insects (Insecta) as well as the cell walls of fungi. Chitosan, a polyelectrolyte derivative of chitin. This polysaccharide, obtained from renewable resources, is currently being explored intensively for applications in the pharmaceutical, cosmetics,

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biomedical, biotechnological, agricultural and food industries, and in non-food applications as well water treatment, paper and textile. Chitosan is an antibacterial, biocompatible, environment-friendly, biodegradable material and has great potential for sorption of metal ions due to amino and hydroxyl groups in its chemical structure. The physico-chemical properties of chitosan are related to the presence of amine functions that make it very efficient for binding cations from near neutral solutions. The sorption capacity of chitosan is mainly controlled by its degree of deacetylation which influences the physical, chemical and biological properties of chitosan, such as acid–base and electrostatic characteristics, biodegradability, self aggregation, sorption properties and the ability to interact with metal ions.

The chemical modification of natural or synthetic polymers is an elaborate experimental task that improves the original surface properties of the materials for use in academic and technological applications. The modification of natural polymers is a promising method to yield new materials having special properties that enlarge the field of the potential applications of biopolymers. Various investigations have demonstrated the effectiveness of chitosan and its derivatives in the uptake of metals, such as lead, copper, cadmium, nickel and oxyanions, as well as complexed metal ions. Various methods have been used to modify chitosan in order to improve its sorption capacity. The large number of primary amino and hydroxyl groups at the second and sixth positions with high reactivity enables a variety of chemical modifications. Chitosan has been attractive because the free amino groups in this modified product contribute polycationic and chelating properties and has recently been subjected to many chemical modifications to produce advanced functional materials. This chemically modified chitosan has greater uptake capacity for heavy metal ions such as mercury, chromium, copper, zinc, tin, cobalt, nickel, lead, mercury and cadmium (Saha and Orvig, 2010; Rojas *et al*, 2005; Padmaja, 2011; Gulay, 2006, Kushwaha, 2011). This paper will report the making of chitosan from shrimp shell and its application on trace metals determination in environmental samples.

## II. Experimental Method

Chitin was isolated from prawn and shrimp shell. Chitosan (2-amino-2-deoxy-(1→4)-β-D-glucopyranan), a polyaminosaccharide, was obtained by alkaline deacetylation of chitin (Figure 1). Colorimetry method using Etylen DiammineTetraAcetate (EDTA) was used for determination of Cu, and *diphenyl thiocarbazone* (ditizone) was used for Zn. Detailed analytical method was following the colorimetric method written in Vogel, 1989 and Firdaus, 2007. Chemical reactions of complex formation are as follow:

$$Cu^{2+} + EDTA^{2-} \rightarrow Cu(EDTA)$$

$$Zn^{2+} + 2ditizone^{2-} \rightleftharpoons [Zn(ditizone)_2]^{2-}$$

The blue color of Cu complex and the red color of Zn complex were then analyzed by spectrophotometry method (Spectronic 21D, Thermo) at wavelength 580 nm and 520 nm, respectively. All experiments were conducted in a batch system (Cheng, 2011).

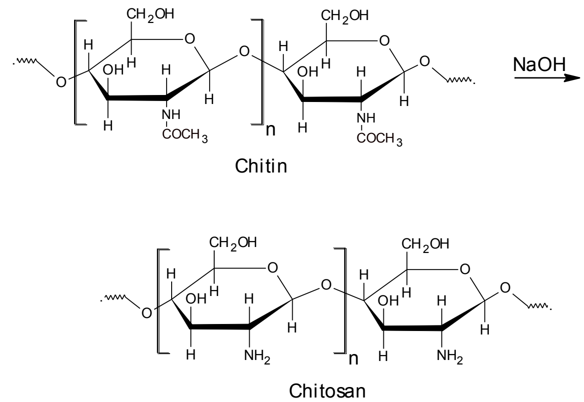



Fig. 1 Synthetic scheme to produce chitosan from chitin using alkaline deacetylation method

## III. Results And Discussion

The specification of home-made chitosan is shown in Table 1.

TABLE I
COMPARISON OF HOME-MADE CHITOSAN WITH THOSE OF QUALITY STANDARD CHITOSAN

| Parameter | Quality Standard | Present Study |
|---|---|---|
| Particle Form | Shard to Powder | Shard |
| Water Content (%) | ≤ 10.0 | 4.57 |
| Ash Content (%) | ≤ 2.0 | 1.93 |
| Color | White | Yellowish White |

Water content of 4.57% meets the quality standard of chitosan. Chitosan is hygroscopic which has the ability to absorb moisture in the air around 230-440%. Factors that must be considered in order to produce low moisture content is drying, packaging and storage conditions of the chitosan. Therefore, the produced chitosan must be stored in closed containers. Ash content of 1.93% chitosan is within the range allowed by quality standard. Ash content shows the number of remaining mineral content in the material. Low ash content of chitosan is one factor that led to high levels of purity. Low ash content also indicates that the demineralization process is successful.

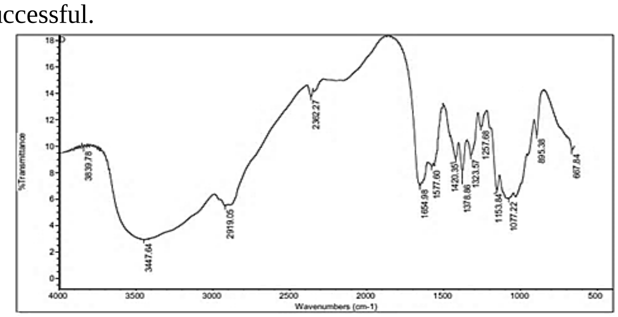



Fig. 2 FTIR Spectra of home made chitosan

Figure 2 shows the FTIR spectra, the peak around 3447, 64 $cm^{-1}$ is assigned to the stretching vibration of hydroxyl groups (-OH). The peak at 2919,05 $cm^{-1}$ is assigned to the to the stretching vibration of C-H group. And the peak around 1654,98 $cm^{-1}$ and 1378,86 $cm^{-1}$ are assigned to the stretching vibration of N-H group and C-H group. The sorption capacity of chitosan is mainly controlled by its degree of deacetylation, from the calculation know that the degree of deacetylation of the chitosan obtained for 63.9%.

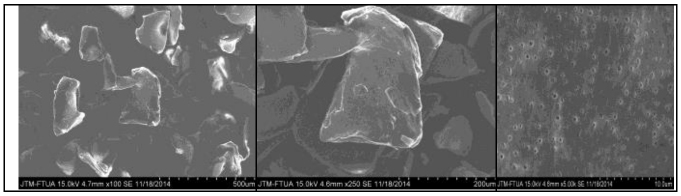


Fig. 3 SEM photomicrographs of chitosan

Scanning electron microscopy (SEM) is used to characterize the morphology of the chitosan surface, shown in Fig. 3. It is found that the surfaces of chitosan flat with irregularly shape and porous. The average diameter of home-made, shown is 5 µm.

The sorption of elements using biopolymers such as chitin and chitosan is one of the reported emerging biosorption methods for the removal, even at low concentration (ppm or ppb levels). Chitin and chitosan are abundant, renewable and biodegradable resources. Chitin, a naturally occurring mucopolysaccharide, has been found in a wide range of natural sources such as crustaceans, fungi, insects, annelids and molluscs. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, crayfish) primarily because a large amount of the crustacean exoskeleton is available as a by-product of food processing. The annual worldwide crustacean shells production has been estimated to be 1.2 x $10^6$ tonnes, and the recovery of chitin and protein from this waste is an additional source of revenue. Utilization of industrial solid wastes for the treatment of wastewater from another industry could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy (Guo *et al*, 2009).

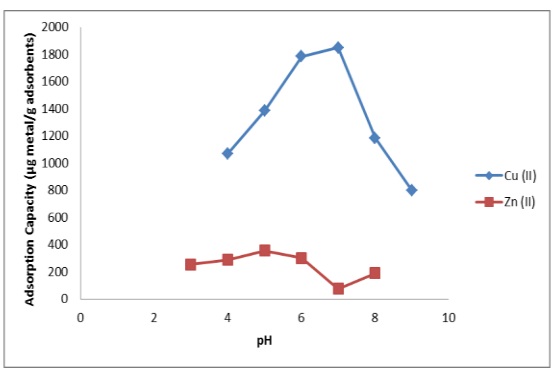



Fig. 4 Adsorption capacity of Cu (II) and Zn (II) for various pH

Figure 4 shows adsorption capacity of Cu (II) and Zn (II) for various pH. Decrease in adsorption capacity occurs after the optimum point, shows that the equilibrium of Cu (II) and Zn (II) are capable of adsorbed by chitosan has been exceeded. Chitosan sorption of metal ions due to amino and hydroxyl groups in its chemical structure.

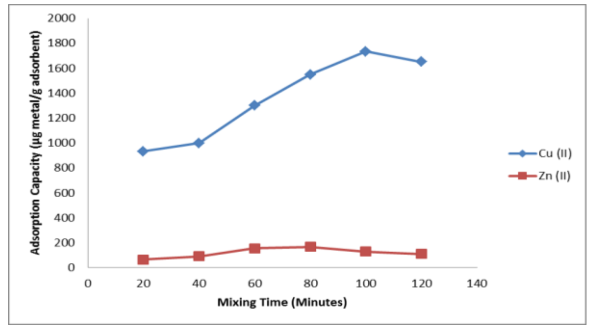



Fig. 5 Adsorption capacity of Cu (II) and Zn (II) for various mixing time

Figure 5 shows adsorption capacity of Cu (II) and Zn (II) for various mixing time. Adsorption capacity of Cu (II) onto chitosan were higher than Zn adsorption onto Chitosan. Figure 5 shows the optimum mixing time of Cu onto chitosan occurs in 100 minutes with the adsorption capacity for Cu (II) is 1733.3 g/g adsorbent. While Zn adsorption onto chitosan, has the optimum mixing time occurs in 80 minutes with the adsorption capacity of Zn (II) is 167.3 µg/g of adsorbent.

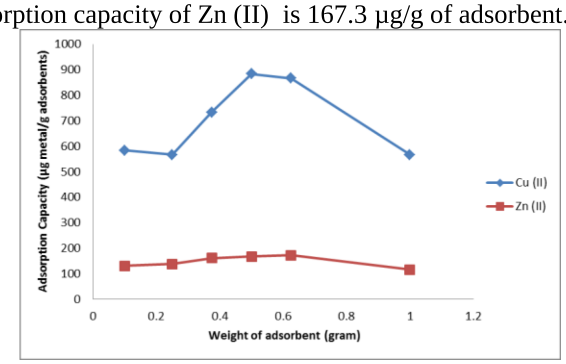



Fig. 6 Adsorption capacity of Cu (II) and Zn (II) for various adsorbents concentration

The increase in weight of the adsorbent will provide more active sites thereby increasing the percentage of adsorption. Determination of the weight of adsorbent was conducted using uniform adsorbate concentration equal to 100 mg/L with optimum mixing time obtained in previous treatments. Figure 6 shows the results of adsorption capacity of Cu (II) and Zn (II) for various adsorbent concentration. We found that chitosan gives a higher adsorption capacity for of Cu (II) than Zn (II).

Chitosan has drawn particular attention as a complexing agent due to its low cost compared to activated carbon and its high contents of amino and hydroxy functional groups showing high potential for adsorption of a wide range of molecules, including phenolic compounds, dyes and metal ions. This biopolymer represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, excellent chelation behavior and high selectivity toward pollutants (Chojnacka, 2010).

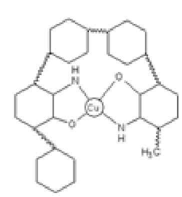
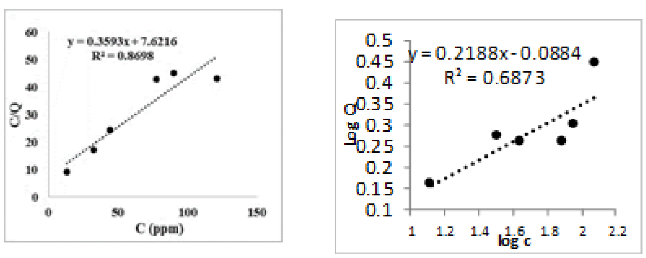


Fig. 7 Proposed bonding mechanism of chitosan and Cu

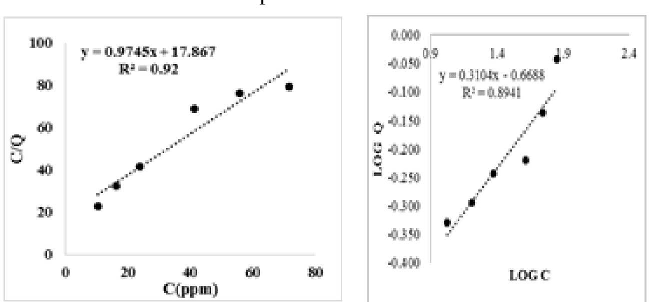
The study demonstrated that chitosan-based biosorbents are efficient materials and have an extremely high affinity for many elements. They are also versatile materials. This versatility allows the sorbent to be used in different forms, from flake-types to gels, bead-types or fibers. The proposed bonding mechanism is shown in Figure 7. Functional groups of amine and hidroxyl provide excellent bonding agent for interest elements such as Cu (II).

Determination of isotherm adsorption is used to study the adsorption mechanism of adsorbate by adsorbent. Adsorption can be described by a relationship between the amount of adsorbate per unit weight of adsorbent in the equilibrium concentration. Figure 8a and 8b show result of Langmuir and Freundlich isotherm adsorption onto chitosan for Cu and Zn. From the value of $R^2$ we conclude that both metals tend to be adsrbed chemically than physically which is the characteristic of Langmuir isotherm.




(a) (b)

Fig. 8a Isotherm Adsorption Langmuir (a) and Freundlich (b) for Cu adsorption onto Chitosan




(a) (b)

Fig. 8b Isotherm Adsorption Langmuir (a) and Freundlich (b) for Zn adsorption onto chitosan

Chitosan from shrimp shells as a bioadsorbent can remove heavy metal Cu (II) and Zn (II) in aquatic samples, shown in the table below. Aquatic samples from lake water, estuarine water, river water, and PDAM water in Bengkulu City, Province of Bengkulu, Indonesia.

TABLE II
MEASUREMENTS OF CU (II) AND ZN (II) CONCENTRATION IN AQUATIC SAMPLES IN BENGKULU CITY

| Sampel | Cu (II) | | | Zn (II) | | |
|---|---|---|---|---|---|---|
| | $C_{first}$ (ppm) | $C_{last}$ (ppm) | Eff (%) | $C_{first}$ (ppm) | $C_{last}$ (ppm) | Eff (%) |
| Lake Dendam | 0,8 | 0,6 | 33,3 | 6.5 | 2.4 | 62.9 |
| Bangkahulu estuarine | 0,6 | 0,3 | 50,0 | 4.3 | 2.0 | 52.2 |
| Hitam river | 1,1 | 0,8 | 25,0 | 2.8 | 1.3 | 53.3 |
| PDAM water | 0,3 | 0,0 | 100,0 | 1.1 | 0.7 | 33.3 |

## IV. CONCLUSION

We have synthesized and tested the ability of chitosan as a chelating resin for reduction of Cu (II) dan Zn (II) concentration in aquatic samples. The preference of chemisorptions nature of Cu (II) dan Zn (II) onto chitosan than those of physisorption probably cause in high adsorption capacity of chitosan for selected metals. Chitin and chitosan are underutilized natural polymers. Although cost effective isolation remains difficult primarily because raw material sources not consolidated or stabilized, derivation of chitosan produces a remarkably diverse group of potential products, primarily as chelating resin, which can be stored for long periods, thus giving high economic value for chitosan.

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