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# ADSORPTION ISOTHERMS OF LEAD ION BY CHITOSAN FROM SHRIMP SHELL

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***ABSTRACT***
*The adsorption activities of chitosan from dried shrimp shells Metapenaeus monoceros (Fabrices)has been studied by analyzing its ability to remove lead ion from aqueous solution. This process including (i) isolation of chitosan from shrimp sells by deproteinization with NaOH, demineralizationby adding HCl solution, decolorizationwith sodium hypo chlorideand deacetylation by adding NaOH, (ii) studied of interaction between chitosan and Pb. The qualitative and quantitative method were used to analyses this chitosan.The isolate of chitosan has 72.39 % degree of deacetylation. This isolate was added intolead solution 10 – 1000 mg/l at pH 5. Furthermore, the solutions were shaken during 24 hours. After separation of chitosan from solution, the filtrate was identified by using Atomic AdsorptionSpectrophotometric. The results showed that chitosan from dried shrimp shells can used as adsorbent of lead ion at pH 5 which followed Freundlich isotherm (r > 0.95).*

***Keywords*** *:adsorption, chitosan, Metapenaeus monoceros (Fabrices), lead ion*

## INTRODUCTION

Pollution in our life increase day by day. The sources of pollutions may come from industries, vehicles and waste houses. The effect of pollution causes negative impact for air, soil even of water. Waste metal is the most important pollution because it is can't be biodegradable. The growth of waste metal toxic contamination in environment were caused by increasing industrial activities and human's life style. Bounding waste metal with organic materials produce complex compounds which have toxic effect for living organisms (Tarigan & Rozak, 2003). One of the most comment metal ions which has persistent to contaminate the environment is lead metal ion (Pb) because its non-degradable disposition. Lead metal is usually produced by waste of industries of drycell battery, paint,ceramicmanufacture, and also the vehicle emissions(Sanjaya, 2001).Nowadays researcher concern to study the best ways to prevent or decreasing the number of lead metal inthe environment.The obvious reason was lead

ion is toxic for most living thing and it can't be degradable in nature (Badmus,*el.al*, 2007).The accumulation of lead at environment cause damaging brain of young children, malfunctioning of digestion, and blood stream(Naria, 2005).

Common method for decreasing the number of lead metal from environment is adsorption as suggested processfor economically viable reason. Some articles have been report the advantages of this method for removal heavy metal at environment, pervade efficient, wildly applicable and relatively little sludge(Bernard, E., and Jimoh, 2013).

Adsorption is the adsorb process of solid and gas substances bythe surface of adsorbent. It is passed off depend on bonding type. Each materials adsorbent containing variety functional groups which would be attached by chemical bonding(Kusmiyati,*et,al*, 2012). The process of adsorption is cover up the adsorbent surface with molecule layer, the capacity was depend on characteristic of adsorbent, concentration and temperature of the molecules adsorption(Malik, *et,al*, 2006). If some adsorbent was added into solution, it would increase the amount substance at surface adsorbent and concentration of solution until equilibrium between adsorption and desorption rate(Shrestha, *et,al*, 2013).

Material for adsorbent was chosen by the wide surface and mass transfer ability in order to separate samples and adsorbent maximally (Kusmiyati , *et,al*, 2012). Adsorbent is made from bioorganic material or waste of home industries that can be potential to be used. One of material for adsorbent is chitosan. Chitosan is derivate of chitin which isa biopolymer fund in crustaceans. Chitin currently used as medicals application such as supplement dietary because of its fat adsorbing capability, materials for bandages to prevent bleeding, or controlling blood cholesterol(Burrows,*et,al*, 2007).

Chitosan has amino and hydroxyl functional groups which effectively bound the cation of metal ions became complex compound and by comparison with chitin, chitosan is capable for making membrane for the adsorbent substance (Agustina, 2008).

Shrimp is one of large export commodity from marine resources in Indonesia. Waste of shrimp production process such as shells, heads and tails which has been benefited maximal can be used for source of chitosan by isolation treatment. Shrimp shells consist of protein, calcium carbonate and chitin, which content depend on the species of shrimp(Candra *et,al*, 2008).

The isolation process of chitosan has been report in two methods, biological and chemical methods(Arbia, *et,al*, 2013). This research in order to evaluated physical and chemical properties of the isolate of chitosan from dried shrimp shells to be used as adsorbent of lead metal ions solution. Enhance the utilization of shrimp shells and minimize waste shrimp pollution at environment.

## MATERIAL AND METHOD

### Materials

Atomic Adsorption Spectrophotometric (Merk GBC 932 AA), Fourier Transform Infra Red Spectrophotometric FTIR (Perkin-Elmer Spectrum One), shaker, analytic weight (Metler PM 2000), filter papers, Phmeters E 520 (MetrohmHerisau) Trinoculer microscope (Carton), oven (Sharp), Furnace, thermometer, sieve 250 μm, water bath, blender and the glasses ware.

Chitosan (SIGMA® 116H1465), sulphate-acid, nitride acid, Pub(II)nitrate, chloride acid, acetone, sodium hydroxide, sodium hypo chloride, calcium carbonate, magnesium carbonate.

*Samples preparation*

Shrimps waste was got from Tanah Kongsi fish market Padang West Sumatra. The process begins with cleaning shrimp shell, sun dried for two days and cut it into small pieces. Samples were characterization at Ecology Laboratory Biology Faculty ofAndalas University, and the dried shrimp shells was from Metapenaeus Monoceros Fabrice's, which usually found at Indonesian waters. It was identified by the rude tough of shells and brown light color.

## Experimental

*Isolation chitosan*

Isolation chitosan refers to Hong method (Khan,*et,al*, 2002;Agustina et al., 2008)First deproteinization dried shrimp shells by adding sodium hydroxide 3.5 % at temperature 65°Cfor two hours. The residuewas washed until neutral pH. Then it continued by carried out chloride acid 1N into residue for 30 minutes, purified chitin by washed with water. The next process was carried out by adding acetone 1: 60 for an hour. Residue was colorless by adding sodium hypo chloride 0.315% for 30 minutes and drained off.

Deacetylation process carried out by addingsodium hydroxide 60% 1: 20 at temperature 100°C for an hour. Crude chitosan dried for 4 hours and powdered into 250 μm sieve.

## Characterization of chitosan

Characterization of chitosan from the isolation process consist of the following measurement:

*Loss on drying*

The measurement was determined by gravimetric method. Chitosan were heat in to the oven at 105°C until constant weigh

Loss on drying

$$=\frac{wight\ chitosan\ after\ dryed}{wight\ sample\ chitosan}\ x\ 100\%$$

*Ash measurement*

Sample chitosan was heated in furnace until became charcoal, then it was added by sulfate acid and heated at 800°C until the ash became white powders.

$$\text{Ash value} = \frac{weight\ of\ residue}{weight\ of\ sample}\ x\ 100\%$$

*FTIR identification*

Dried powder chitosanandKBrwascrushed till homogenous, and pressed in to a thickness pallet. IR spectra functional group of chitosan was obtained with FTIR Spectrophotometric Perkin-Elmer. The result was compared with chitosan (SIGMA® 116H1465).

*Degree of deacetylation DD*

Degree of deacetylation chitosan was determined inbase line method(Khan et al., 2002)by compare adsorption wave at 1665 $cm^{-1}$ and 3450 $cm^{-1}$

$$DD = 100\left(\frac{A_{1665}}{A_{3450}}\ x\ \frac{100}{1,33}\right)$$

$A_{1665}$and $A_{3450}$were the adsorbent of amine 1665 $cm^{-1}$and N-acetyl group at 3450 $^{cm-1}$. 1,33 was the value which denoted of ratio $A_{1665}/A_{3450}$for fully N-acetyl chitosan. Ratio of the deacetylation chitosan was a rectilinear between N-acetyl and amine group (Khan et al., 2002)

*Protein identification*

Biuret test is used for finding out chitosan free from protein by violet color did not appear.

*Content of Ca and Mg ion*

The isolate of chitosan was added by HCl solution and after 30 minutes separate it from residue, then the filtrate was measured by Atomic Adsorption Spectrophotometric at 422,7 nm for Ca ion and 285,2 nm for Mg ion. Make the calibration curve between standard and sample solution.

*Distribution of particles*

Particle size was measured by using microscope particle.

*Adsorbs lead ion with chitosan isolation*

Analysis with batch method, chitosan was added to lead solution in difference concentration at pH 5, the solution was shaken for 24 hours and separate it with sieve. The filtrate was added $HNO_3$. Lead ion which is not absorbed by chitosan was identified with Atomic Adsorption Spectrophotometric, Isotherm adsorption lead metal ion based on Freundlich and Langmuir state that connectivity concentration with adsorption substance.

Freunlich $\text{Log } C_{ads} = \log P + \frac{1}{n} \log C_{eq}$

Where Cads was amount of Pb adsorbed ($mg \cdot g^{-1}$), Ceq was equilibrium concentration in solution ($mg \cdot dm^{-3}$), 1/n was Freundlich constant ($mg \cdot g^{-1}$), and Pwas Freundlich constant ($g \cdot dm^{-3}$)(Ramasubramaniam,*et,al*, 2012)

Langmuir $\frac{C_{eq}}{C_{ads}} = \frac{1}{b.C_{max}} + \frac{C_{eq}}{C_{max}}$

where $C_{max}$ (mg $g^{-1}$ ) was the maximum amount of metal ions adsorbs per unit weight of adsorbent to form a complete monolayer, $C_{eq}$ (mg $L^{-1}$ ) is the equlibrium concentration of the solution and $C_{ads}$ (mg $g^{-1}$ ) (Moganavally,*et,al*, 2015)

## RESULT AND DISCUSSION

Chitosan was a biopolymer which was used to adsorb lead metal from solution through the physic and chemical mechanism. Polysaccharide such as hydroxyl and amine from chitosan was the functional groups which could be bounding the metal ion(Younes & Rinaudo, 2015).

First chemical method of isolation chitosan from dried shrimp shells was deproteinization with sodium hydroxide. Protein which has covalent boundwith chitinresoluble in base solution became Na-protein which solute by water(Ridhay, 2016). Sodium hydroxide at high concentration and temperature will acceleratethe bounding of protein and NaOH so that the degradation process and the precipitation of proteins became perfection.(Agustina et al., 2008)

Dried shrimp shells consist ofprimary of minerals inorganic such as calcium carbonate(Marganof, 2003). Demineralization process was used to reduce mineral salts by adding chloride acid solution.

$2\ HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2\uparrow$

The result of demineralization from chitin was identified by appeared the gas carbon dioxide. Then salts were separated by filtration of solid chitin and washing with deionizer water (Kusumaningsih, Masykur, & Arief, 2004). The demineralization process was dependingon the acid solution selection. IslemYounesreport that using of formic acid was most aforementioned than chloride acid, but drastic treatment may cause modification such as depolymerization and deacetylation of native chitin. Using chloride acid under 2 to 3 hours stirring was the most achieved method than longer demineralization time would cause polymer degradation,(Younes & Rinaudo, 2015).

The quality of chitin isolation may decrease if still had the pigment colored in it. To remove the pigment is usually use weak oxidation such as sodium hypo chloride. Chitin isolation were identified by reaction iodin from KI to the isolation and gave brown colored which became violet after adding sulfate acid (Agustina et al., 2008)

The transport process of chitosan from chitin calls deacetylation. This process is useful to remove ethyl groups from chitin by adding high concentration of alkali. In this experiment we use sodium hydroxide 60% at 100°C for 60 minutes. The amine group of chitin were hydrolyzed became amine group, the product were chitosan and acetate (Agustina et al., 2008).

The Combination of high concentration of alkali solution and stirrer at high temperature as long as deacetylation process, influence the value deacetylation degree and the quality of isolate of chitosan (Hossain & Iqbal, 2014). The isolate of chitosan was identified include the description, rendement of transformation chitosan from percent of chitosan to chitin samples.Loss on drying was determined by gravimetric method

| No | Evaluation | Qualify | Observation |
|---|---|---|---|
| 1. | Organoleptic | White yellow powders, testeless, smell less | White yellow powders, testeless, smell less |
| 2. | Loss on drying | Maximum 10 % | 2.099 % |
| 3. | Ash value | Maximum 2 % | 0.3699 % |
| 4. | Protein identification | Biuret test became violet | Violet didn't appear |
| 5. | Content of | | |
| | • Ca | | - 0.1619 % |
| | • Mg | | - 0.0702 % |

The FT-IR studies with standard chitosan (SIGMA®116H1465) with range spectrum 4000-400 $cm^{-1}$. The adsorption bands of isolate of chitosan were identical to those of standard chitin. Stretching vibration bands were observed in range 3500-3100$cm^{-1}$ related to O-H bond, 3000-2900$cm^{-1}$ indicated C-H bond 2877$cm^{-1}$ were C-H for aldehyde, and 1700-1600$cm^{-1}$ for C=O bond. The spectrum of isolate of chitosan was compared the standard could be indicated that the isolation of chitosan from shrimp shell was success.

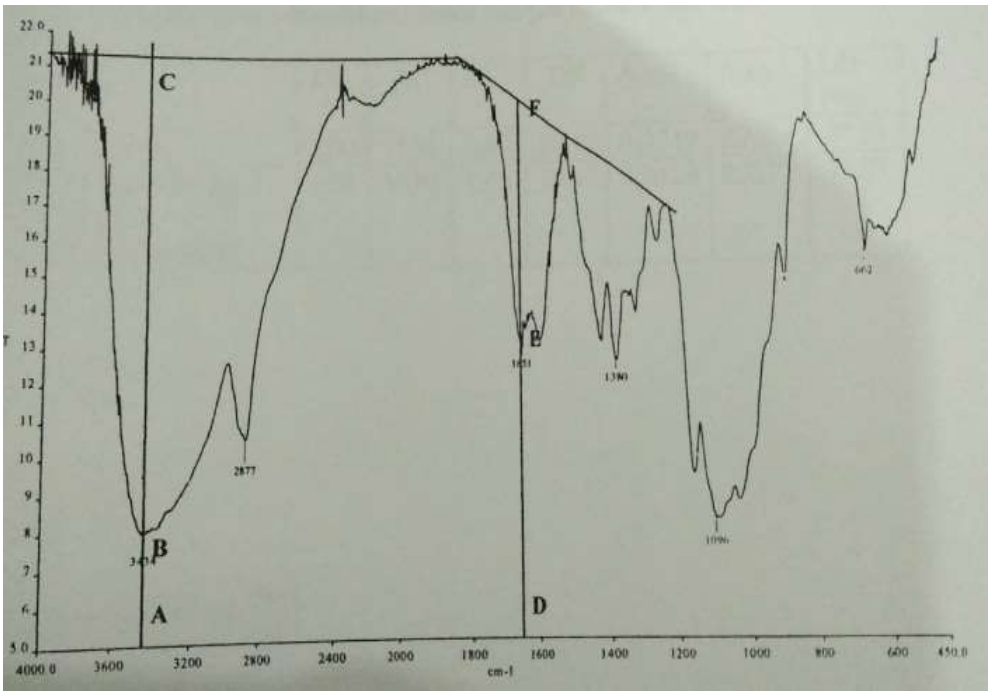


Figure 1. FT-IR of isolate of chitosan

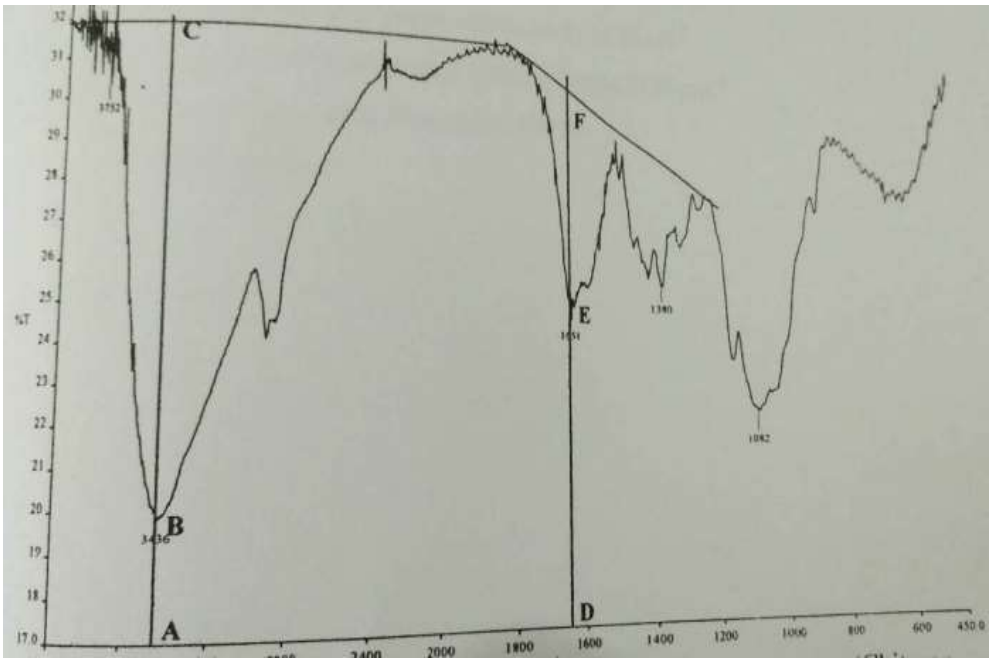


Figure 2. FT-IR chitosan standard

The degree of deacetylation of chitosan were related to adsorption bond of wave light 1655cm$^{-1}$and 3450cm$^{-1}$. Wave light 1655cm$^{-1}$ is the adsorption of carbonyl N-Acetyl and 3450cm$^{-1}$ for hydroxyl polysaccharide (Zvezdova, 2010). DD of chitosan were determined by base line method and calculate with equation according Baxter et.al which modification by Domzy and Robert, DD of isolate of chitosan were 72.39% and it have been compatibility with standard from literature as same or as 70% (Khan et al., 2002).

Distribution of particle was identifiedby using microscope particle for seeing particle size, the average of particle chitosan was got at 116,489 µm. According to Farmakope Indonesia third edition, the thin powder ofisolate of chitosan had standardization for adsorption lead metal ion.

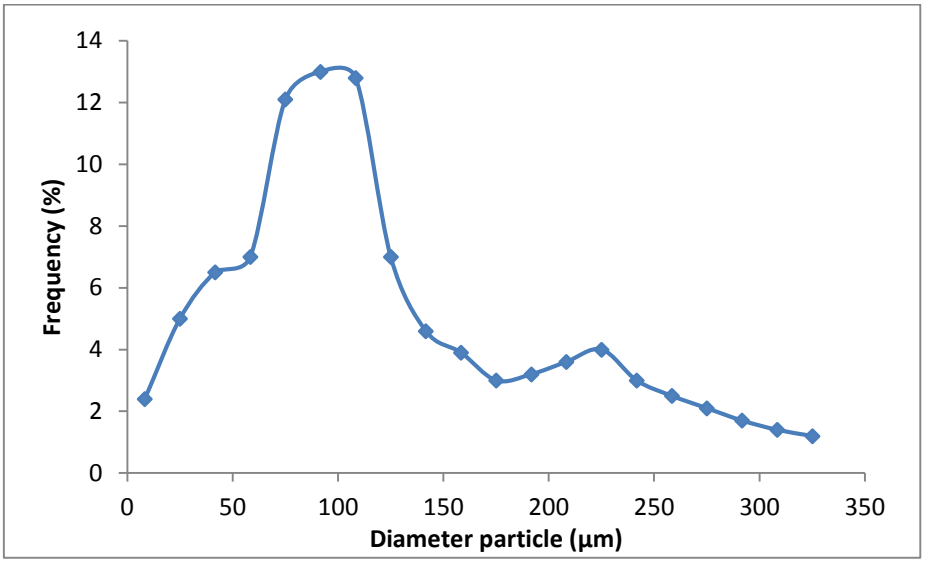


Figure 3. Frequency of particle size of chitosan

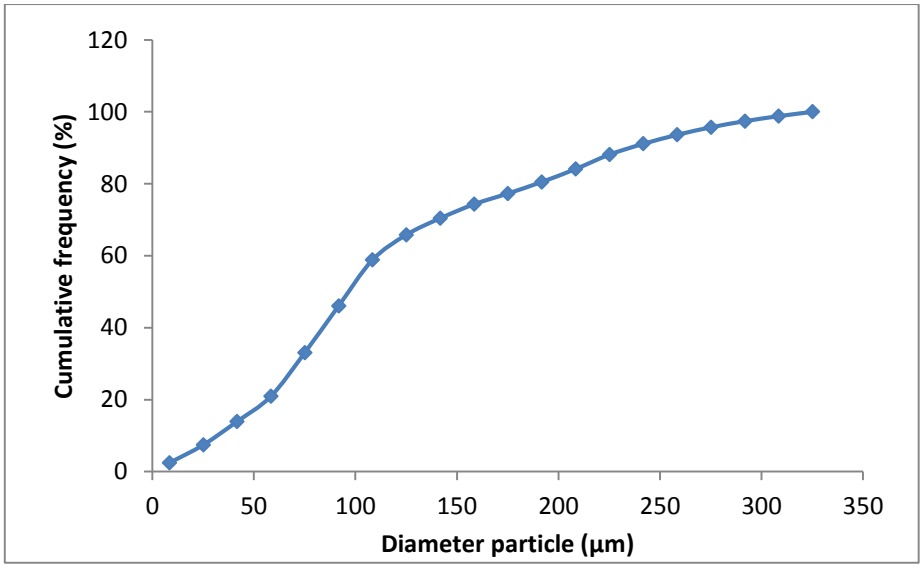


Figure 4. Cumulative frequency of particle size of chitosan

Adsorption process was detected by adding some of lead solution pH 5 toisolate of chitosan. The mixture was shaken at 200 rpm for 24 hours. The process was continued by separating the adsorbate and filtrate, lead ion which did not adsorb by chitosan and still at the filtrate was identified using Atomic Adsorption Spectrophotometric. This method is based on relationship between of amount beam energy which adsorb by lead ion from sample (Sikanna, 2015). Parameters for determined the optimum adsorption was depend on pH solution at constant temperature, concentration metal ion and adsorbent (Moganavally et al., 2015).

Concentration of lead ion which did not adsorb by the chitosan was determined with calibration curve, linier concentration and adsorbent at the straight line. Samples solution was determined the adsorption and calculated into calibration curve.

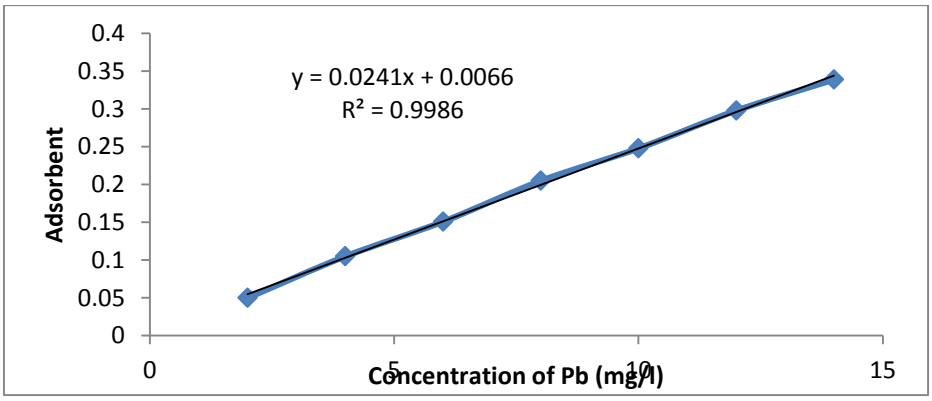


Figure 5. calibration curve standard solution of lead ion in $HNO_3$solution,

Amount of lead ion which adsorb by the chitosan was increase with enhance concentration to 10;50;100;200;500 and 1000 mg/l of lead ion solution at pH 5. More concentration of lead solution was more lead ion which could adsorb by the chitosan. At experiment was got 7;21;31;71;123;and 209 mg/l lead ion was adsorb at variation concentration. If the concentration lead solution was increased, chitosan would adsorb more of lead ion, so it was difficult to determine the adsorption capacity of chitosan at lead ion.

Linear plot of curve amount adsorbent every grams of chitosan and logarithm equilibrium of samples concentration were obtained freundlich adsorption isotherm. Coefficient correlation of Freundlich isotherm was 0,9853 ± 0,0001. And for Langmuir isotherm, coefficient correlation was 0,8923 ± 0,0052.

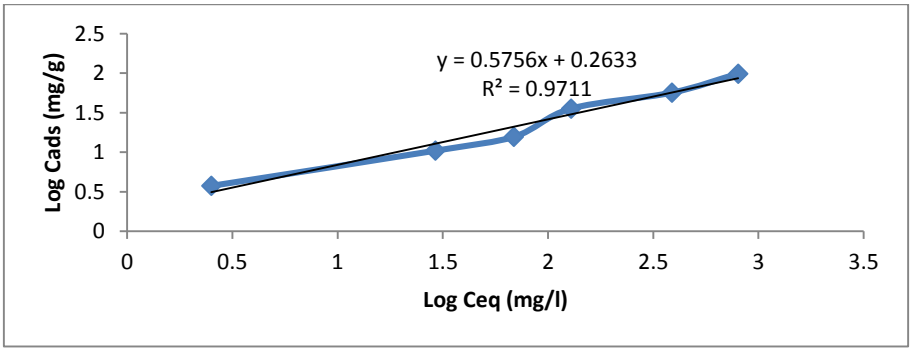


Figure 6. Isotherm curve of adsorption lead ion by chitosan at pH 5 using Freundlich isotherm

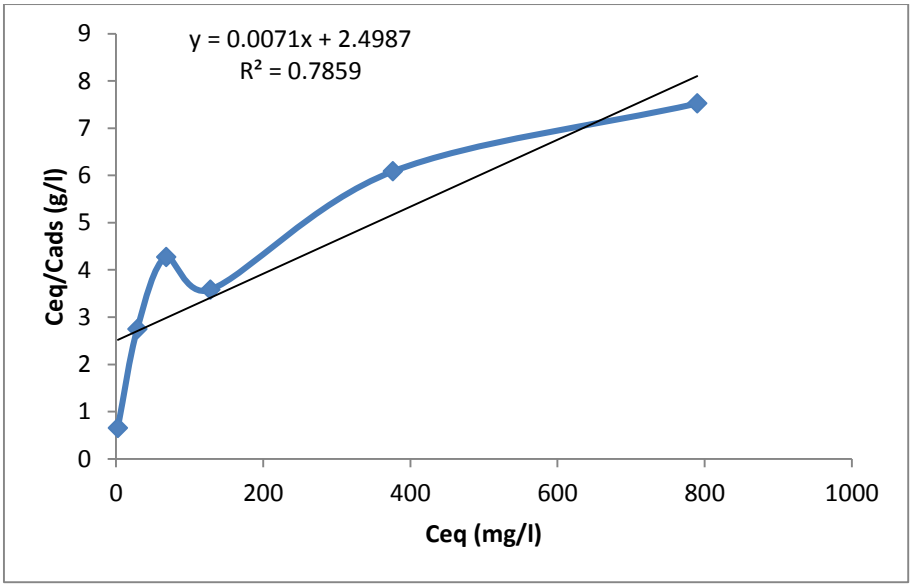


Figure 7. Isotherm curve of adsorption lead ion by chitosan at pH 5 using Langmuir isotherm

Differenced of coefficient correlation between both of isotherm method was significant.The adsorbent of lead ion at pH 5 was followed Freundlich isotherm (r > 0,95). Kinetic adsorption from isotherm Freundlich which P and 1/n was refers to adsorption intensity and capacity was about 1,8227 ± 0,0168 g/l and 0,5815 ± 0,0065 mg/g each of them.

## Conclusion

Process isolation of chitosan from shrimp shells consist of deproteinization, demineralization, decolorization and deacetylation. Isotherm adsorption of lead ion by chitosan at pH 5 was followed Frendlich isotherm, not for Langmuir isotherm.

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