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Adsorption of Cd(II) Metal Ion on Adsorbent beads from Biomass *Saccharomyces cereviceae* - Chitosan Hasri¹ & Mudasir² ¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Parangtambung, Makassar, Indonesia ²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta, Indonesia, 55281 hasriu@unm.ac.id Abstract.

The adsorbent beads that was preparation from *Saccharomyces cereviceae* culture strain FN CC 3012 and shrimp shells waste and its application for adsorption of Cd (II) metal ion has been studied. The study start with combination of *Saccharomyces cereviceae* biomass to chitosan (Sc-Chi), contact time, pH of solution and initial concentration of cations.

Total Cd(II) metal ion adsorbed was calculated from the difference of metal ion concentration before and after adsorption by AAS. The results showed that optimum condition for adsorption of Cd(II) ions by Sc-Chi beads was achieved with solution pH of 4, contact time of 60 minutes and initial concentration adsorption 100mg/L. The hydroxyl (-OH) and amino (-NH₂) functional groups were believed to be responsible for the adsorption of Cd(II) ions. 1.

Introduction Decreased levels of heavy metal waste, especially waste of waters have become a serious concern of various parties. In line with the several methods have been made in reducing the presence of heavy metals such as waste reduction methods, precipitation, ion exchange method, coagulation, solvent extraction, reserve osmosis, adsorption or in combination with other [1][2].

However, the adsorption method is simpler easily applied and cheaper in terms of cost. Adsorption methods made from natural materials, is now experiencing rapid development especially materials focused on material that has a high affinity, selectivity and ability to absorb metal cations in particular [3]. One of promising adsorbent material is using microorganisms as adsorbent.

The use of microorganisms is very promising considering both living and dead microorganisms has the ability to accumulate metals, because the cell wall composed of polysaccharides, lipids and protein which is carboxylic group, hydroxyl, sulfhydryl, phosphates and amino acids that able to binding metal ions [4]- [8]. On the other side, the selection matrix of chitosan as a supporter of microorganisms, additionally the chitosan resources that abundant especially on crab and shrimp waste, non-toxic and the results showed that the chitosan has active sites such as OH, NH₂ and -NHCO-, this group can form chelates with metal cations.

Microorganisms such as *S. cereviceae* as adsorbent has higher surface area that is suitable for absorption of cations [9]. In addition, biomass *S. cereviceae*, either dry (dead) and dead have the same 2 ability and easily decomposed. Technically biomass very difficult to used repeatedly for low mechanical strength. Therefore, it needs to be modified to overcome the shortage of biomass.

Through the combination with chitosan, it is possible to improve the mechanical properties, chemical properties, increasing the porosity and the application can increase the ability to absorb metal cations [10]. The combination of both active sites of the adsorbent and suitable characteristics metal ion is an important factor in progress adsorption takes place [11]. 2.

Methods 2.1. Materials Shrimp shell waste (*Penaeus monodon*) was obtained from P.T. Kima, Makassar. Pure culture of *S. cereviceae* strain FN CC 3012 was a collection of Microbiology Laboratory, (PAU), Universitas Gadjah Mada, Yogyakarta. Reagents in analytical grade comprising Cd(NO₃)₂, HCl, NaOH, CH₃COOH. Distilled water and double distilled water were acquired from the Chemistry Laboratories, UGM.

2.2. Equipments Includes chemical glass, hot plates, analytical balance (OHAUS), Atomic Absorption Spectrometer (Perkin Elmer Model 5100 PC). 2.3. Experimental Section 2.3.1. Microorganism production. Pure culture of *S. cereviceae* . It was maintained on potato glucose agar at 30°C. To produce biomass powder, a 100 ml of potato glucose medium was inoculated in the 250 ml conical flasks with spore suspension and grown in submerged culture conditions.

Biomass of mycelium harvested, by filtration from the growth medium and washed several time using doubly distilled water. The obtained biomass was dried at 60°C. Further processing, the powders 100 mesh. 2.3.2. Combination of *S. Cereviceae*. Chitosan was prepared from shrimp shell waste through deproteination followed by demineralization and deacetylation processes according to the method reported earlier (Gadd, G. M., and White, C., 1993). Amount of chitosan powder mixture of *S. cereviceae* (0,100 gram) was completely dissolved in 20 ml of 2% (w/w) acetic acid.

The adsorbent Sc- Chi were stirred slowly for 30 minute, then washed with distilled water until the solution became neutral. characterized using an FTIR (Shimadzu Prestige-21), X-ray diffraction electron, EDX (Shimadzu XRD-6000). The adsorbent after combination (Sc-Chi) were dried and stored before use. 2.3.3. Preparation of Metal Stock Solution.

Metal solutions were prepared by diluting 1000 mg/l of Cd²⁺ solution with double distilled water to make concentration range from 10 to 200 mg/l. Each solution, the initial Cd(II) concentration and the concentration in the samples after adsorption experiment were determined using an atomic absorption spectrometer. 2.3.4. Adsorption studies. Adsorption of Cd(II) ions onto Sc-Chi from aqueous solution was investigated in batch experiments.

The effects of the pH, contact time, the initial concentration of Cd(II) ions, and absorption capacity were also studied. 2.3.5. Effect of pH. On the sorption rate of Sc-Chi adsorbent were investigated in the pH from 2,0 to 9,0. Using volume 10 ml of Cd(II) ions solution 100 mg/l. The pH of the solution was adjusted using 0,1M HCl and 0,1M NaOH.

0,1gram of Sc-Chi adsorbent were transferred to this medium and the reaction mixture was stirrer for 60 minute. Uptakes of Cd(II) ions were determined from the difference of Cd(II) in the initial and final solution. The Cd(II) ions concentration, the samples was analyzed using an atomic absorption spectrophotometer (AAS) 3 2.4.

Data Analysis The amount of metal ion adsorbed by using adsorbent obtained by using the following expression: $q = (C_0 - C_e)V/m$ (1) q is the amount of metal ion adsorbed onto the unit amount of the adsorbent (mg/g). C_0 and C_e are the initial and equilibrium concentration of Cd(II) ion (mg/l) after sorption, respectively. V is the volume of the adsorption medium (l) and m is the amount of the adsorbent (g).

The empirical Langmuir equation which is valid for monolayer sorption onto a completely homogeneous surface is given by equation 2: $q_e = q_{max}K_c C_e / (1 + K_c C_e)$ (2) where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium

metal ion concentration in the solution (mg l^{-1}), q_{max} is the maximum monolayer sorption capacity of the adsorbent (mg g^{-1}), and K is the Langmuir sorption constant (l mg^{-1}) related with the free energy of sorption [8][12][13].

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy. The equation representing Freundlich model is: $q_e = K_f C_e^n$ (3) Model Freundlich assumption: where K_f is a constant relating the sorption capacity and n is an empirical parameter relating the sorption intensity, which varies with the heterogeneity of the material [14]. 3.

Result and Discussion The weight ratio between the biomass *S. cereviceae* ratio on chitosan done with a variation of 0% to 100%, the highest adsorption was obtained at a ratio of 10%. The composition is an ideal composition, each functional group either chitosan or *S. cereviceae* means adsorbent Sc-Chi has been optimized in binding metal ions Cd (II). Figure 1. Ratio Chitosan with *S. cereviceae* after interaction with Cd(II) ions Adsorption Cd(II), mg g^{-1} Ratio *S. cereviceae*, b/b (%) 4 Figure 2.

Infrared spectrum of adsorbent Sc-Chi before and after interaction with Cd(II) ions. Results of FTIR spectra biomass *S. (Sc)* shows the absorption peak at 3387 cm^{-1} as the -OH group and the -NH of polysaccharides are overlapped, the absorption peak at 1651 cm^{-1} supported a peak at 1033 cm^{-1} indicates the group C = O carboxylic asymmetry and stretching vibration cm^{-1} indicates the group NH although not sharply (Figure 2).

Based on the results of the identification FTIR spectra known that biomass *S. cereviceae* (Sc) has -OH groups, -COOH and -NH₂. It is supported by Gadd, G. M., 1990, states that immobilization cell support matrix for example; alginate, poliakrilamide, and chitosan has a high adsorption efficiency, although the diffusion restriction would be a problem Gadd and white, 1993; Tobin et. All., 1994). The study used by Sc-Chi adsorbent ratio of 10%. *S. cereviceae* XRD analysis results are as follows: 1,9; 9o ..

peak to (Cat ? 2,2 then biomass *Saccharomyces cerevisiae* ($Sw_2 = 80$, Afmdied amedthe o iffn eaks t ? 18o crystal structure of the (100). This reinforces the information that modification Sc-Chi has occurred,, the diffraction pattern is between the two adsorbents. Figure 3. Diffractogram X-Ray of *S. cereviceae*, chitosan and adsorbent Sc-Chi. 5 Figure 4.

EDX adsorbent Sc-Chi before and after interaction with Cd(II) The characterization results on EDX spectra (Figure 4), the adsorbent constituent elements Sc-Chi showed sharper spectra and growing constituent elements. 3.1. Effect of pH Acidity (pH) represent important factor which have an in with metal ion adsorption process in condensation effect of active site or H⁺ ion competition of cation for binding of active

site, at the same time have an effect on to metal ion interaction with active site. Figure 5.

Effect of pH on Sc-Chi adsorbent, Cd(II) 100mgL⁻¹; sample volume of 10 ml; time contact 60 minute. Figure 5. The sorption of Cd(II) increase as the pH increased. This is likely due to the protonation of the functional groups on the Saccharomyces cereviceae immobilized on chitosan structure [10]. At higher pH of 2,0, the sorption quantity increased up to pH of 6,0.

At higher than 7,0, Pb(II) ions precipitated out because of high concentration of OH- ions [7][8]. 3.2. Effect of Contact Time Maximum Cd(II) ions sorption with Sc-Chi adsorbent was initial period of contact time up to 60 minute. After that decreased amount of Cd(II) ions in solution Cd(II) uptake,mgg - 1 pH ScChi Chi Sc 6 Figure 6.

Effect of contact time on Sc-Chi adsorbent, Cd(II) 100mgL⁻¹; sample volume of 10 ml. This rapid sorption stage indicate that surface sorption occur on Sc-Chi adsorbent. The extent of adsorption efficiency increases sharply with time and attains equilibrium at about 60 minute 3.3. Effect of Initial Cd(II) Ion Concentration The sorption of Cd(II) ion Sc-Chi adsorbent was carried out at different initial Cd(II) ion concentration 10 - 200 mgL⁻¹.

Figure 7. Effect of initial concentration on sorption of Cd(II) ions on Sc-Chi adsorbent; volume of 10 ml; time contact 60 minute. Adsorption of Cd(II) ions was increased as the initial concentration up to 25mgL⁻¹, all Cd(II) ions present in solution could interact with binding site. Nearly 100% adsorption was observed when concentration increased from 10-25 mgL⁻¹.

This could be because at higher concentration, as more ions are competing for the available binding sites [10]. Analysis in the of the isotherm data is important in order to develop an equation. Adsorption isotherm also describes how solutes interact with adsorbent and so is critical in optimizing the use of adsorbent.

The lead uptake capacity of Sc-Chi adsorbent was evaluated using pseudo order-2 adsorption isotherm. Table 1. The number of reaction rate constant (k) and the correlation coefficient (R²) metal ion adsorption kinetics model of Cd (II) Kinetics Model Reaction rate constant (k) Sc-Chi R² Orde-1 0,006 min⁻¹ 0,434 Ion logam teradsorpsi (mg/g) Time (minute) Adsorption Cd(II) mgg - 1 Concentration, mgL⁻¹ Sc-Chi Sc Chi 7 Kinetics Model Reaction rate constant (k) Sc-Chi R² Orde-2 20,45 M min⁻¹ 0,356 Orde pseudo-2 0,035 g mol⁻¹min⁻¹ 0,995 Table.

1 shows that the pseudo-second-order more appropriate with the Sc-Chi adsorbent

because forming the linear regression than model of kinetics first order and order-2, this indicates that the adsorption of metal ions Cd (II) following model of pseudo kinetics second order. The reaction rate constant of Sc-Chi adsorbent larger than before modification, the amount of adsorption rate due to the number of active group that acts on the adsorbent Sc-Chi unequal or crowding so that the reaction rate is slower than the biomass of *Saccharomyces cereviceae* Sc, but chitosan shows the adsorption rate same with an adsorbent Sc-Chi, this is likely due to the active site that play a part in adsorbing metal ions Cd (II) is not much different. 4.

Conclusion The result of research showed that optimum condition of adsorption of Cd(II) ion by Sc-Chi adsorbent with ratio of 10%, pH of solution of 7, contact time of 60 minutes and initial concentration adsorption 25mg/l-1. This adsorbent can be a good candidat for adsorption of not only Cd(II) ions but also other heavy metal ions in wasterwater stream.

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