

Biosorption of heavy metal copper (Cu^{2+}) by *Saccharomyces cerevisiae*

S A J Ririhena, A D Astuti, M F Fachrul, M D S Silalahi, R Hadisoebroto, A Rinanti*

Environmental Engineering Department, Faculty of Landscape Architecture and Environmental Technology, Universitas Trisakti, Jakarta

*Corresponding Author : astririnanti@trisakti.ac.id

Abstract. This research aims to study the optimum effect of contact time and pH adsorption of copper (Cu^{2+}) from electroplating industry waste by dried beer waste *S.cerevisiae*. This research conducted using batch culture with pH variation 2,3,4,5, and 6, contact time variation 60, 90, 120, 150, 180 minutes, 150 rpm at room temperature ($\pm 28^\circ\text{C}$), initial Cu^{2+} concentration 33,746 mg/l, and biosorbent mass 200 mg & 500 mg. The adsorption of heavy metal ions Cu^{2+} occurs in all variations of pH and contact time at optimum pH. The optimum adsorption occurs at pH 4 with contact time 120 minutes for both 200 mg (41.60%) and 500 mg (61.04%) beer waste biosorbent. Cell morphology seen with Scanning Electron Microscope (SEM) analysis shows the change of cell wall that gets damaged from Cu^{2+} adsorption. It also proved by the decreased concentration of initial high concentration carboxyl groups. The adsorption process of this research complies to Freundlich Isotherm with R^2 value closest to 1 and followed first order kinetic.

Keywords: contact time, copper, pH adsorption, *S.cerevisiae*

1. Introduction

Various research regarding metal ion reduction treatment has been done, such as oxidation-reduction, precipitation, adsorption, compaction, electrolytic recovery, and ion exchange. These processes are expensive in which some technological problems exist especially when applied to diluted metal solutions. Therefore, the search for clean and competitive technologies is strongly recommended. Biological treatment is usually considered as an effective method and can significantly reduce the quantity of heavy metals in aqueous solutions [1]. Study of biosorption as an alternative treatment considered effective in cost and easy to apply. Biosorption can adsorb more heavy metals than chemical precipitation on bigger pH range [2]. Biosorption capacity is mainly influenced by three kinds of influential factors: metal ionic characteristics (e.g., atomic weight, ion radius, valence) the nature of the biosorbents (e.g., cell age), and biosorption conditions (e.g., pH, temperature, contact time) [3].

This research aims to study the effect of contact time and pH to adsorption of Cu^{2+} ion by biosorbent *S. cerevisiae*, determine the adsorption efficiency of Cu^{2+} ion contain in electroplating wastewater by biosorbent *S. cerevisiae*, and determine functional groups involved in Cu^{2+} adsorption process.



2. Research Method

2.1. Biosorbent Preparation

S. cerevisiae that found in beer waste can be used as biosorbent. Beer waste centrifuged at 3600 rpm for 60 minutes. Biomass that formed in the bottom of centrifuged tube collected into a petri dish and then put it in the oven with temperature 80°C for 28 hours to let it dry. Dried biomass then grind with mortar and passed through screener (30 mesh) until it becomes powder.

2.2. Industrial Electroplating Wastewater Characterization.

Characterization utilized with *Atomic Absorption Spectrophotometry* (AAS).

2.3. Cu^{2+} adsorption on pH variation

Dried biosorbent of 200 mg and 500 mg were put into 70 mL electroplating wastewater contained Cu^{2+} then solution pH was adjusted to variation 2, 3, 4, 5, and 6. After that the solution was put on shaker 150 rpm for 90 minutes. Then the solution was centrifuged with 4000 rpm for 30 minutes to separate biomass with the solution. The concentration of Cu^{2+} remainder in solution determined by *Atomic Absorption Spectroscopy* (AAS) analysis.

2.4. Cu^{2+} adsorption on contact time variation

Dried biosorbent of 200 mg and 500 mg were put into 70 mL electroplating wastewater contained Cu^{2+} in optimum pH. After that, the solution was put on a shaker with 150 rpm for a specific variation of contact time 60, 90, 120, 150, and 180 minutes. The solution then was entrifuged with 4000 rpm for 30 minutes to separate biomass with the solution. The concentration of Cu^{2+} remainder in solution determined by *Atomic Absorption Spectroscopy* (AAS) analysis.

3. Results and Discussion

The result of electroplating wastewater characterization indicates that it contained 33,764 mg/L Cu^{2+} without any other metals detected.

3.1. Determining Optimum pH

The potential of hydrogen (pH) is one of the main factors that affects biosorption process. Metal ions adsorptions depends on solution pH, which influences electrostatic binding of ions to corresponding functional groups [4].

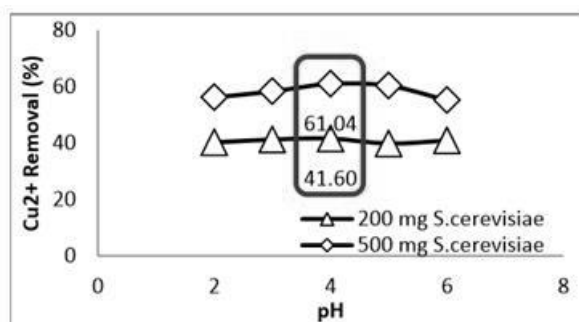


Figure 1. Effects of pH variation towards Cu^{2+} removal (%) at contact time 90 minutes, room temperature ($\pm 28^\circ\text{C}$), and Cu^{2+} initial⁺ concentration 33,746 mg/L.

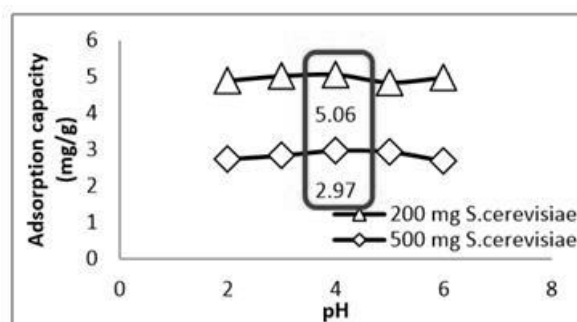


Figure 2. Effects of pH variation towards adsorption capacity (mg/g) at contact time 90 minutes, room temperature ($\pm 28^\circ\text{C}$), and Cu^{2+} , initial concentration 33,746 mg/L.

Based on Figure 1 Cu^{2+} adsorption efficiency increased from pH 2 until pH 4 which has the highest adsorption efficiency for all biosorbent samples whereas at pH 5 until pH 6 Cu^{2+} removal efficiency decreased and has the lowest removal efficiency. It correspond with previous study that shows the optimum adsorption for Cu^{2+} ion happens at pH 4 until 5 [5]. The adsorption of heavy metal Cu^{2+} occurs

because of ions exchange mechanisms between heavy metal ions and carboxyl groups, phosphate, and amino which are the main components of *S.cerevisiae* cell wall, capable of acting as ion exchangers and complex formers with metal ions. At the low pH, concentration of protons is high and the ion exchange sites become solidly protonated, therefore metal adsorption will occur better at low pH [6].

As seen in Figure 2, the highest adsorption capacity also happen at pH 4, which compatible with previous study said the removal efficiency of Cu^{2+} occurs at a maximum of 3 g/L or 3 mg/mL biosorbent concentration but the removal efficiency will decrease if there is additional biosorbent concentration used [7]. This may occur due to the presence of biosorbent bundles that cause a decrease in surface area for adsorption, resulting in decreasing adsorption capacity. Previous study report at pH 4.5 200 mg *S. cerevisiae* adsorb 2,042 mg/g Cu^{2+} [8]. Based on these things it can be concluded that pH 4 is the optimum pH for biosorbent *S. cerevisiae* to adsorb Cu^{2+} .

3.2. Determining Optimum Contact Time

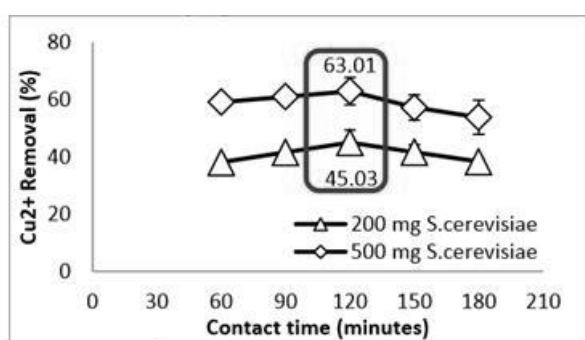


Figure 3. Cu^{2+} removal (%) towards contact time variation (minutes) at pH 4 (optimum), room temperature ($\pm 28^\circ\text{C}$), and initial Cu^{2+} concentration 33,746 mg/L.

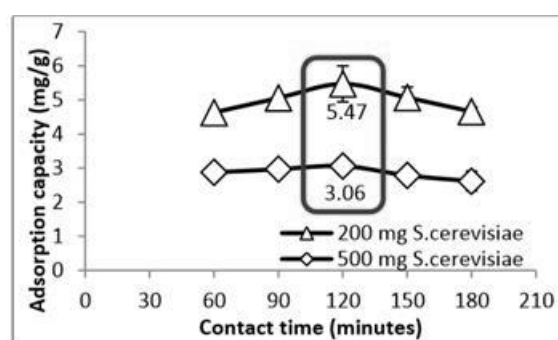


Figure 4. Adsorption capacity (mg/g) towards contact time variation (minutes) at pH 4 (optimum), room temperature ($\pm 28^\circ\text{C}$), and initial Cu^{2+} concentration 33,746 mg/L.

Based on Figure 3 Cu^{2+} removal efficiency keeps increasing until optimum at 120 minutes and decreasing at contact time 150 minutes. Previous study shows that optimum contact time for Cu^{2+} removal happened at 90 minutes and stay stable until 120 minutes [8]. 500 mg biosorbent *S. cerevisiae* has larger surface area than 200 mg *S. cerevisiae*, therefore 500 mg *S. cerevisiae* has higher Cu^{2+} removal efficiency than 200 mg *S. cerevisiae*.

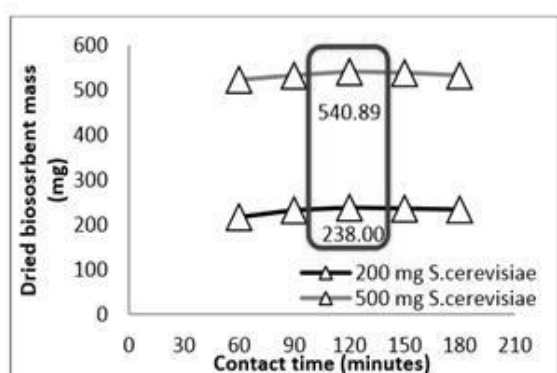


Figure 5. Dried biosorbent mass (mg) towards contact time at pH 4 (optimum), room temperature ($\pm 28^\circ\text{C}$), and initial Cu^{2+} concentration 33,746 mg/L.

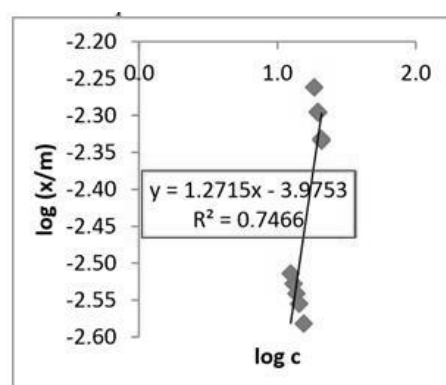


Figure 6. Isotherm Freundlich.

The same tendency can be seen in Figure 4, adsorption capacity for 200 mg biosorbent *S. cerevisiae* is in the range 5-6 mg/g with highest capacity at 5.47 mg/g at and for 500 mg biosorben *S. cerevisiae* is in the range 3 mg/g with the highest capacity at 3.06 mg/g at optimum pH and contact time.

Figure 5 shows a correlation between dried bisorbent mass with contact time. Initial 200 mg dried biosorbent mass increased up until 238.00 mg while initial 500 mg increased up to 540.89 mg. The increasing dried biosorbent weight occurs due to heavy metal ion Cu^{2+} presence from solution that adsorb into biosorbent *S. cerevisiae* in accordance with the quantity Cu^{2+} adsorb from solution into biosorbent *S. cerevisiae* cell wall, other than that there's a chance of impurities in solution that goes through the filter and weighted together with dried *S. cerevisiae* biosorbent. As contact time increase, the weight of dried biosorbent will increase until the saturation point which is 120 minutes and begin to decrease at 150 minutes and 180 minutes.

3.3. Determining Optimum Contact Time

Adsorption isotherm used to determine the occurrence of Cu^{2+} adsorption characteristic, and a curve will be generated to shows the maximum adsorption capacity of *S. cerevisiae* biosorbent based on the characteristic. Calculation of adsorption isotherm value of this study using Langmuir, Freundlich, and BET isotherm. The use of adsorption isotherms is to determine the most representative description of this study biosorption process.

Langmuir isotherm assumes that adsorbent surface has a certain number of adsorption points which is proportional to the surface area of the adsorbent and adsorption only occurs on the monolayer thus the adsorption process can only occur in the adsorbent that has not been filled by any adsorbate. Whereas for Freundlich Isotherm used to explain non-ideal adsorption process on the heterogeneous surface because of functional groups difference in adsorbent (Figure 6). BET isotherm assumed that adsorbent has homogenous surface and adsorbat molecule can form more than one layer on the surface [9].

From calculation results shown in Table 1, adsorption process of this study follows Freundlich Isotherm with the highest R^2 value between Langmuir and BET Isotherm. R^2 value of Langmuir Isotherm is not so different than Freundlich value, according to Freundlich the adsorbent surface is heterogeneous, composed of different classes of the adsorption region, but each class adsorption follows Langmuir isotherm, therefore the adsorption tends to be similar.

3.4. Adsorption Kinetics

Adsorption kinetics is a study to determined reaction order and speed rate of adsorption process that happened. The reaction of the biosorption rate provides important information to create a batch scale biosorption system. The approach used in calculating the adsorption kinetics in this study is first order and second order.

Table 1. R^2 Value calculation of adsorption isotherm and kinetics.

R^2			R^2	
Isotherm Langmuir	Isotherm Freundlich	Isotherm BET	First Order	Second Order
0.71	0.7466	0.4731	0.0448	0.0351

Based on R^2 value seen in Table 1, the value of first order kinetic adsorption is closer to 1 than second order thus it can be said that the adsorption kinetics that occurs tend to follow the first order. The first-order reaction is a reaction whose velocity depends only on one of the reactive substances which or is proportional to one of the reactant forces [10].

3.5. Analisis Fourier Transfer Infra-Red Spectrophotometer (FTIR)

Biosorbent *S. cerevisiae* has three main functional groups which are carboxyl groups, amino groups, and hydroxyl groups. *S. cerevisiae* cell wall composed of a-mannan and b-glucan, protein, lipid, and inorganic substances particularly phosphate, chitin, and chitosan. Proteins that construct *S. cerevisiae* cell wall are rich in glutamic acid residues, aspartate, serine, threonine, and asparagine. Based on FTIR

analysis it is known that biosorbent *S. cerevisiae* has high carboxylic acid, carboxyl group, and amine. In this FTIR results chitin included in acid carboxyl functional groups which in the 3277/cm area, which indicates the peak of O-H.

The carboxyl group in the 1625/cm region indicates the peak presence of C = O, and amine at 1234/cm indicates the peak presence of N-H. The content of carboxylic acid decreased from 92.27% to 92.04%, carboxyl group decreased from 98.04% to 89.77%, Amine from 94.17% to 92.33%, and alkane from 95.93% to 94.37%. This indicates the presence of functional groups involved in the adsorption of Cu^{2+} ions which cause changes in functional groups in the biosorbent of *S. cerevisiae* either in the presence or the content of functional group present in the biosorbent.

3.6. Scanning Electron Microscope (SEM) Analysis

Scanning Electron Microscope (SEM) is a type of electron microscope that uses a focused beam of high-energy electrons to produce images of a sample by creating a variety of signals at the surface of the sample [11]. SEM produces high-resolution images of a sample surface, capturing a complete size of approximately 1 - 5 nm and can produce 3-dimensional shape characteristics so as to provide easier data about the analysed samples [12].

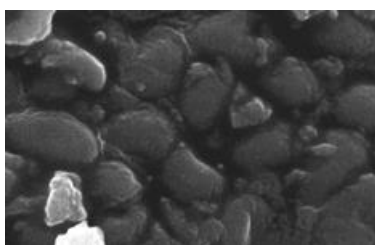


Figure 7. Control *S. cerevisiae* seen with SEM (500x)

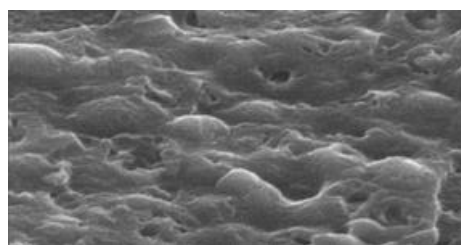


Figure 8. *S. cerevisiae* after contact with Cu^{2+} in optimum condition seen with SEM (500x)

Based on Figure 7 and Figure 8 we can see the difference in cell morphology before and after contact with Cu^{2+} . As seen on Figure 8 *S. cerevisiae* cell wall looks shrivelled and have more holes than before contact (Figure 7) which look more hydrated and plump. This morphological change occurs due to Cu^{2+} ion adsorption process that happened in the cell wall during contact with electroplating wastewater. The change that happened is not too significant because the biosorbent is used in a state of death & dried so no metabolism progress occurs and disturbed by the absorption of Cu^{2+} ions.

4. Conclusion

From this research, we can conclude that contact time and pH affect the adsorption of Cu^{2+} by biosorbent *S. cerevisiae*, with optimum contact time 120 minutes and optimum pH 4. Optimum Cu^{2+} adsorption efficiency happens at pH 4, contact time 120 minutes, 500 mg *S. cerevisiae*, initial Cu^{2+} concentration 33.764 mg/l, at room temperature ($\pm 28^\circ\text{C}$), shaker speed 150 rpm is 63,01%. This research adsorption process follows Freundlich Isotherm with the highest R^2 value between Langmuir and BET isotherm which is 0.7466. Reaction kinetic of this research follows first order kinetics with R^2 value higher than second order value. Several functional groups involved in adsorption of heavy metal Cu^{2+} are carboxyl acid, carboxyl groups, and amine which proved by the decreased concentration of these functional groups.

Acknowledgment

The authors would like to thank Directorate for Research and Community Services as well as Directorate General for Strengthening Research and Development at the Ministry of Research, Technology, and Higher Education Indonesia for funding this study through Universities Prime Research Grant Program (Penelitian Unggulan Perguruan Tinggi-PUPT) 2016.

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