Utilization of wild algae biomass as biosorbent for removal of heavy metal Zinc (Zn\(^{2+}\)) from aqueous solution

Maisarah*, S Adityosulindro and D Wulandari

Civil and Environmental Engineering Department, Faculty of Engineering, Universitas Indonesia, Depok, 16424, Indonesia
*Corresponding author: maisarah91@ui.ac.id

Abstract. Climate change has both a direct and indirect effect on surface water quality. One of them is the increase in chemical weathering which causes the release of heavy metals in aquatic sediments. The toxicity of high concentration heavy metals and the phenomenon of algal bloom also become a threat to the freshwater environment. It is known that several types of algae can live, develop, and act as a biosorption agent for various types of heavy metals. The use of algae-based biosorbent also can reduce the level of global warming from the production of commercial adsorbents such as activated carbon. Hence, the objective of this study was to determine the capability of wild algae biomass from the lake Situ Agathis Universitas Indonesia, Depok West Java as a heavy metal biosorbent by elaborating on its biosorption performance, for the benefit of the wastewater treatment and the management of algae bloom. Removal efficiency zinc improved significantly by activation treatment with thermally and base treatments on wild algae biomass. The result from the experimental laboratory showed that the zinc removal up to 92.12% in 120 min by NaOH activation method at neutral pH. The obtained results suggest that the wild algae biomass is a promising benign and low-cost material for industrial wastewater treatment.

1. Introduction

Since the Industrial Revolution, the production process that produces industrial wastewater cause heavy metals become a major concern in treatment systems [1]. Zinc (Zn (II)), the heavy metal ion as model inorganic contaminant within the present study, is found at higher level in effluents from industries such as electroplating, chemical industry, automotive, dyeing and other industries [2]–[5]. Directly and indirectly, climate change has an effect on the state of surface water. The impact of high temperatures due to increased CO\(_2\) levels will increase chemical weathering and cause a lower pH. So that, this phenomenon will cause the release of metals in the earth crust, soil and sediment [6].

In other problems, environmental pollution has resulted in the phenomenon of algal bloom which occurs as a problem. The abundance that exists in Indonesia can be seen from a number of eutrophication cases that have occurred in Indonesian waters [7], one of which is the lake Situ Agathis Universitas Indonesia Depok, West Java (Indonesia). It is known that several types of algae can act as a biosorption agent for various types of heavy metals. So that by utilizing the algal bloom phenomenon, the algae at this source will be used as an alternative biosorbent in minimizing water pollution [8]. The use of algae-based biosorbent can also reduce the level of global warming from the production of commercial adsorbents such as activated carbon [9].

In this study the type of mixed-culture algae from the lake Situ Agathis Universitas Indonesia Depok was used in a state without cultivation or also called wild algae cultures. Inactive algae biomass was used as a heavy metal removal agent for Zn (II) using the biosorption process. The wastewater treatment method using sorption is preferred because of its easy handling and cost-effectiveness [10].
biosorption process will be influenced by metal affinity, which can be manipulated by pre-treatment of biomass in the form of activation method with alkalis, acids, detergents and heat [11], [12]. Therefore, this study aims to determine the capability of wild algae biomass (WAB) from the lake Situ Agathis Universitas Indonesia, Depok West Java as a heavy metal biosorbent by elaborating on its biosorption performance, for the benefit of the wastewater treatment and the management of algae bloom.

2. Material and method

2.1. Material and reagents
Chemical reagents used throughout this study are all analytical grade reagents. Powdered zinc chloride was obtained from Pudak Scientific (molecular formula: ZnCl\textsubscript{2}·7H\textsubscript{2}O, molecular weight: 136,286 g/mol, solubility: 432 g/100 g water at 25 °C, and purity: 98%). Further, the stock solution of Zinc (1000 mg/L) as well as all the working reagents used during the experimental stage were dissolved using distilled water. NaOH, NaCl, and CaCl\textsubscript{2} (Merck) dilute solution was used as treatment activation. HCl and NaOH (Merck) dilute solution was used to adjust the pH of the solution.

2.2. Biomass preparation
With a total mass of 80.5 g of WAB from algae blooms, it originated at the extraction site in the lake Situ Agathis Universitas Indonesia Depok, West Java (Indonesia) as shown in Figure 1. The sampling procedure using plankton net is based on the procedure written in [13]–[15] on sampling methods. According to Utomo et al., [16], before being used for the biosorption process, the collected WAB samples are washed repeatedly with tap water then with distilled water to remove dirt and other unwanted material. Then the washed WAB was dried in oven at 104°C for 4-6 hours to ensure that the samples are completely dry and reduce their moisture content. The dried WAB was shredded, ground in a mortar, and passed through sieves with pore sizes of 0.25 mm. All dried algae are filtered using sieves so that their size is homogeneous in the form of WAB powder.

![Figure 1. The Lake Situ Agathis Universitas Indonesia Depok, West Java Indonesia.](image-url)

2.3. Preparation of pre-treated biomass
Three different types of treatment were applied to the WAB, namely: (1) treatment with 0.1 M NaOH (AN) [17], (2) heating treatment made in physiological saline solution (NaCl 0.9%) (AH) [18] and (3) treatment with 0.2 M CaCl\textsubscript{2} (AC) [19]. The untreated WAB is referred as AU. In the case of AN, dry WAB was contacted with 0.1 M NaOH (AN) and 0.2 M CaCl\textsubscript{2} (AC) for 2 hours, then washed until pH <10 was reached. Next the pre-treated biomass was dried again at 60°C for 24 h and the resulting powder was stored in a desiccator [17].

2.4. Batch sorption experiment
The batch reactor biosorption experiment (50 mL) was carried out in a 100 mL erlenmeyer flask which was stirred using an orbital shaker (Fisher Scientific IKA™ KS 260 Control) at a speed of 150 rpm for
120 minutes at constant room temperature (30 ± 0.5 °C). The sorbent (0.075 g) was contacted with a metal ion solution (5 mg/L) at a metal pH value of 6.2. To analyze the effect of contact time, under similar circumstances, samples were collected at different time intervals, i.e., 10, 30, 60, 90, 120, and 180 min. Similarly, to observe the effect of pH the initial values of pH of the metal solutions were adjusted to 2.0, 7.0 and 8.0 with 0.1 M HCl or 0.1 M NaOH using a pH meter (The Hanna Instruments HI98107). The mean values were considered from duplicate experiments.

All samples in the experiment were filtered with a 0.45 μm filter. The amount of metal absorbed was calculated from its initial and final concentrations. The removal efficiency was determined using Equation (1).

\[
Removal (\eta) (\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

Where \(C_0\) and \(C_e\) are the concentration of the biosorbate (mg/L) in the initial and final synthetic zinc solutions, respectively.

2.5. Analytical method
At the end of each experiment, the aqueous phases were filtered from the biosorbent and the filtrates obtained with concentrations of the metal ions in the remaining solutions (±50 mL) were analyzed using atomic absorption spectrophotometer (AAS) (type: Xploraa dual using a GBC atomic absorption reader a SavantAA). The concentrations of heavy metals were determined in an air–acetylene flame by AAS as showed in Table 1.

| Heavy Metal (Zn (II)) | Optimal condition | Mode | Wavelength (nm) | Slit width (mm) | CL (Current Ma) | Pressure Air | Flame Characteristic |
|-----------------------|-------------------|------|-----------------|-----------------|-----------------|--------------|---------------------|
| Absorbance            |                   |      | 213.9           | 0.7             | 7.0             | Air (13.50) : Acetylene (2.00) | Lean-blue         |

3. Results and discussion
3.1. Biosorption studies
The result from preparation WAB following the above procedure to form a powdered as shown in figure 2. It can be seen that there are differences in color in different pretreatments, treatment using alkaline (AU and AC) displays a darker color than WAB powder from untreated or heat treatment.

![Figure 2](image_url)

Figure 2. (a) Samples of grinded untreated WAB (AU); (b) Samples of grinded NaOH pre-treatment WAB (AN); (c) Samples of grinded heat pre-treatment WAB (AH); (d) Samples of grinded CaCl₂ pre-treatment WAB (AC).

The biosorption of heavy metal depends on the functional group of cell wall which containing polysaccharides, proteins and lipids [18]. Several mechanisms such as ion exchange, electrostatic
attraction, complexion, etc. occur in metal ion binding reactions [20]. The constituents from algae cell wall is the first barrier encountered by heavy metals in the biosorption process. The carboxyl (-COOH), hydroxyl (-OH), sulfate (SO$_4$), sulfonic acid (-RSO$_3$H), carboxylate (-RCOO), amino acid (-NH$_2$), and thiol (-SH) in the polysaccharides and lipids of the algal cell wall is a key group that contributes to the biosorption process of heavy metal ions [20], [21].

3.2. Effects of the pre-treatment on the biomass
It has been typically observed that algae must be pretreated first before being used as a biosorbent [22]. Activation treatment to surface modification by sodium hydroxide, calcium chloride, and heat with saline solution conducted in this study. Figure 3 presents the relationship between the variations of treatment activation of WAB on the efficiency of metal ion Zn (II) removal. When 0.075 g of AU was contacted to metal solution, only a 2.64 % removal efficiency could be achieved. The biosorption using AC was enhanced and the removal efficiency reached 37.3 %. The heavy metal removal efficiencies of AH and AN reached 45.9 % and 88.4 %, respectively, when 0.075 g was contacted with Zn (II) solution. So that from this comparison, activation treatment will open more functional groups on the biosorbent surface or increase certain functional groups to increase the biosorption capacity when compared to the untreated.

3.3. Effect of time on the biosorption
The experiments were also carried out by determining the optimum contact time, in industry, this time is very important for process optimization [23]. When the system reaches sorption equilibrium, no further biosorption occurs. The WAB was kept in contact with the metal solution for different time periods (10, 30, 60, 120 and 180 min) at room temperature 30°C with Zn (II) initial concentration 5 mg/L and pH 6.2 using NaOH pre-treated WAB. It is evident from figure 4 where the profiles of the Zn (II) removal efficiency versus contact time are plotted. The biosorption rate of Zn (II) is high at the beginning of biosorption and complete saturation were reached at about after 120 min. Therefore, the biosorption time was set to 120 min in further experiment. Reaction rate is rather fast at first and 81%

![Figure 3. Zn (II) removal efficiencies by WAB after the pre-treatments.](image-url)
of total biosorption of Zn (II) occurs in the first 60 min and then proceeds at a lower rate and increase at 120 min by 88%, finally the assumption is no further significant biosorption after 180 min. The assumption is, after this equilibrium period, the amount of Zn (II) ions did not significantly change with time. Similar found according to the literature, the biosorption of heavy metals Cd²⁺ and Cu²⁺ by algae Laminaria japonica occurred rapidly and reached equilibrium in about 120 min [24].

![Figure 4](image-url)

**Figure 4.** Effect of contact time on biosorption of Zn (II).

3.4. *Effect of pH on the biosorption*

The pH is one of the most important parameters of the biosorption of heavy metals or other compounds [25]. The biosorption of Zn (II) by WAB at different pH values is illustrated in figure 5. The removal efficiency of metals ions increased from 11.3% and 92.12 % but then decreased to 84.09% while the pH increased from 2, 7 and 8 respectively. This indicates that the optimal pH for removal Zn (II) was 7. The sorption process decreased with any further increase of pH (> 7). According to Goher et al., [25], the decrease of metal biosorption at higher pH values is related to the presence of metal precipitation in the form of metal hydroxides due to the ease of reaction of metal ions with OH⁻ ions.

![Figure 5](image-url)

**Figure 5.** Effect of pH on biosorption of Zn (II).

On the other hand, when the pH value is low (pH = 2), the H⁺ concentration is high, then H⁺ will competitively exchange cations on the surface of algae. As the solutions pH increases, the process is reversed, metal ions will start to replace hydrogen ions. Furthermore, when the pH is neutral (pH = 7),
there is an increase in surface deprotonation of the biosorbent causing a decrease in \( \text{H}^+ \) ions on the surface of the biosorbent. So here will be more negative charge on the surface of the biosorbent [25].

4. Conclusions

The results obtained in this study demonstrated that the WAB from the Situ Agathis Universitas Indonesia, Depok West Java is a promising biosorbent material for zinc removal from aqueous solutions. The biosorption of heavy metal ions by WAB was strongly dependent on the pre-treatment. The modified biosorbent presented best results in Zn (II) biosorption by NaOH pre-treatment at pH 7 and contact time 120 min. It is important to note that a change in the pH of the sorption system could significantly alter the removal efficiency. So with these results, the use of natural-derived WAB can also be used as an alternative adsorbent to support the reduction of climate change rates from commercial adsorbent production.

The use of waste algae from the algal bloom as raw material is a relevant alternative for disposal of this waste and even enables added value to waste which is normally disposed of. However, the further approaches are required in the influence of other parametric effect to reach the optimum conditions for removal of heavy metals by WAB. Future studies also can further probe the climate change impacts and toxicity impacts strategy of this biosorbent from lifecycle perspectives. It is hoped that our work can guide the research on the treatment of heavy metal pollution by using WAB.

Acknowledgement

The authors are thankful to Universitas Indonesia for supporting this project for the use of Situ Agathis lake, Depok, West Java as a study object for the source of algae biomass. We also thank the Laboratory of Health and Environmental Engineering, Universitas Indonesia (TPLUI) for providing facilities and resources for carrying out this study.

References

[1] Mohammed A A, Najim A A, Al-Musawi T J and Alwared A I 2019 Adsorptive performance of a mixture of three nonliving algae classes for nickel remediation in synthesized wastewater J. Environ. Heal. Sci. Eng. 17(2) 529–38
[2] Abas S N A, Ismail M H S, Kamal M L and Izhar S 2013 Adsorption process of heavy metals by low-cost adsorbent: A review World Appl. Sci. J. 28(11) 1518–30
[3] Nassef E and Eltaweel Y 2019 Removal of Zinc from aqueous solution using activated oil shale J. Chem. 2019 4261210
[4] Wang H, Wang H, Zhao H and Yan Q 2020 Adsorption and Fenton-like removal of chelated nickel from Zn-Ni alloy electroplating wastewater using activated biochar composite derived from Taihu blue algae Chem. Eng. J. 379 122372
[5] Asfaram A, Ghaedi M and Ghezelbash G R 2016 Biosorption of Zn2+, Ni2+ and Co2+ from water samples onto Yarrowia lipolytica ISF7 using a response surface methodology, and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) RSC Adv. 6(28) 23599–610
[6] Frogner-Kockum P, Göransson G and Haeger-Eugensson M 2020 Impact of climate change on metal and suspended sediment concentrations in urban waters Front. Environ. Sci. 8 1–14
[7] Damar A, Hesse K J, Colijn F and Witner Y 2019 The eutrophication states of the Indonesian sea large marine ecosystem: Jakarta Bay, 2001–2013 Deep. Res. Part II Top. Stud. Oceanogr. 163 72–86
[8] Maisarah, Saebumillah A and Ambarsari H 2020 Study of microalgae (Scenedesmus Sp.) utilization as phosphate bioremediator (PO43-) in domestic wastewater medium IOP Conf. Ser. Mater. Sci. Eng. 763 012055
[9] Nishikawa E, da Silva M G C and Vieira M G A 2018 Cadmium biosorption by alginate extraction waste and process overview in Life Cycle Assessment context J. Clean. Prod. 178 166–75
[10] Hidayat A E, Moersidik S S and Adityosulindro S 2021 Adsorption and desorption of zinc and
copper in acid mine drainage onto synthesized zeolite from coal fly ash  IOP Conf. Ser. Earth Environ. Sci. 1811 012045

[11] Ahalya T V R N and Kanamadi R D 2003 Biosorption of heavy metals Res. J. Chem. Environ. 7(4) 71–9

[12] Kemala D, Moersidik S S, Adityosulindro S and Hilwa F 2019 Enhancing lead adsorption in waste lubricant oil with activated clay as bleaching earth MATEC Web Conf. 276 06020

[13] Hallegraeff G, Anderson D M, Hole W and Cembella A 2003 Manual on Harmful Marine Microalgae: Monograph in Oceanographic Methodology no. 33. (Paris, France: UNESCO Publishing)

[14] Tangen K 1978 Sampling techniques: Net. Phytoplankton manual (Paris, France: UNESCO Publishing) vol. 19 no. 4

[15] Francoeur S N, Rier S T and Whorley S B 2013 Methods for sampling and analyzing wetland algae Wetland Techniques: Volume 2: Organisms eds Anderson J T and Davis C A (Berlin, Jerman: Springer Science+Business Media Dordrecht) p 332

[16] Utomo H D, Tan K X D, Choong Z Y D, et al. 2016 Biosorption of heavy metal by algae biomass in surface water J. Environ. Prot. (Irvine., Calif). 7(11) 1547–60

[17] Shin W S and Kim Y K 2014 Biosorption characteristics of heavy metals (Ni2+, Zn2+, Cd2+, Pb2+) from aqueous solution by Hizikia fusiformis Environ. Earth Sci. 71(9) 4107–14

[18] Arica M Y, Tüzün I, Yağcı E, Ince Ö and Bayramoğlu G 2005 Utilisation of native, heat and acid-treated microalgae Chlamydomonas reinhardtii preparations for biosorption of Cr(VI) ions Process Biochem. 40 (7) 2351–8

[19] Lee H S, Suh J H, Kim I B and Yoon T 2004 Effect of aluminum in two-metal biosorption by an algal biosorbent Miner. Eng. 17 (4) 487–93

[20] Mishra V 2014 Biosorption of zinc ion: A deep comprehension Appl. Water Sci. 4 (4) 311–32

[21] Cheng S Y, Show P L, Lau B F, Chang J S and Ling T C 2019 New prospects for modified algae in heavy metal adsorption Trends Biotechnol. 37(11) 1255–68

[22] He J and Chen J P 2014 A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools Bioresour. Technol. 160 67–78

[23] Montazer-Rahmati M M, Rabbani P, Abdolali A and Keshtkar A R 2011 Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae J. Hazard. Mater. 185 (1) 401–7

[24] Liu Y, Cao Q, Luo F and Chen J 2009 Biosorption of Cd2+, Cu2+, Ni2+ and Zn2+ ions from aqueous solutions by pretreated biomass of brown algae,” J. Hazard. Mater. 163(3) 931–8

[25] Goher M E, El-Monem A M A, Abdel-Satar A M, et al. 2016 Biosorption of some toxic metals from aqueous solution using non-living algal cells of Chlorella vulgaris J. Elem. 21(3) 703–14