

Preparation of Pellet Biopolymer Polyvinyl Alcohol/Alginate/Gluutaraldehyde Impregnated with Banana Peel Activated Carbon (BPAC)

N. I. Inda*, V. Pato, G. Maereka, H. Sosidi, P. Satrimafitrah

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Tadulako University, Palu, Indonesia

Information

Article history:

Received: 27 September 2022

Accepted: 29 December 2022

Published: 31 December 2022

Keywords:

Banana Peel Activated Carbon

Pellet Biopolymer

PVA/Alginate/Gluutaraldehyde

Abstract

Pellet Biopolymer Polyvinyl Alcohol/Alginate/Gluutaraldehyde impregnated with BPAC has been successfully synthesized. The morphology of pellet biopolymer was observed using SEM and mechanical strength of pellet was investigated using Hydraulic Impact Resistance. The density of pellet was also investigated. The result shows that the pellets have a round shape, springy texture, and water content presence inside the pellet. Pellet biopolymer without BPAC have a white gel-like bead, pellet with 0.5 g of BPAC was dark gray, and pellet with 1 g of BPAC was light gray. The SEM images show that the pellet biopolymer with BPAC has a dense surface area than pellet without BPAC. The amounts of BPAC impregnated into the pellet biopolymer affected the morphology of pellet biopolymer. The SEM image of pellet biopolymer with 0.5 g of BPAC shows that the BPAC existed on the surface of pellet biopolymer. However, the SEM image of pellet biopolymer with 1 g of BPAC shows that almost all of the BPAC coated into the pellet biopolymer. The hydraulic impact resistance shows that the amounts of BPAC impregnated into the pellet biopolymer affected the mechanical strength of the pellet, by considering the increasing of pellet biopolymer density. The obtained pellet biopolymer impregnated with BPAC could adsorb the copper (II) ion from aqueous solution.

*) e-mail: nov_chemuh@yahoo.co.id

DOI: 10.22487/gravitasi.v21i2.16039

1. INTRODUCTION

Biopolymer is a polymer material which widely used as an encapsulant and mostly for drug delivery. Based on the shape, there are many types of biopolymers, one of them known as pellet or bead because the round shape of the material. Pellet biopolymer has also been widely used as an adsorbent for metal ion adsorption (Solgi et al, 2020, Singha and Guleria, 2014, Rodriguez et al, 2006, Inbaraj, et al 2009, Vijaya et al, 2008). Pellet biopolymer itself can be considered as an adsorbent by considering the existence of functional group attached on the surface of the pellet biopolymer. Recently, many researchers are using this pellet biopolymer as a coating material for chelating agent (Kalyani, et al, 2005, Vitali, et al, 2006, Fertahi, et al, 2021, El Hankari, et al, 2019). The purpose of the chelating agent coated into the pellet biopolymer is to minimize the adsorbate loss during the separation process and also to ease the separation process. Solvent extraction is generally a liquid-liquid extraction and is really difficult to separate between the aqueous phase and organic phase. In order to minimize the loss during the separation, many researchers developed the liquid-solid extraction method by using an adsorbent as a solid phase (organic phase) and liquid

phase for adsorbate (aqueous phase). However, many of the adsorbent in solid phase have a micro or nanosize. The small size of adsorbent cause the suspension of the adsorbent into the water and lead to the difficulty in the separation process. Therefore, the particle size of the adsorbent is necessarily needed to be improved by impregnated into the pellet biopolymer.

In this research, banana peel activated carbon (BPAC) will be used as an adsorbent and alginate (Alg) will be used as pellet biopolymer because the ability in hydrogels formation (Xiao, et al., 2019). However, alginate is a water soluble compound by considering the hydrophilicity of the alginate. Therefore, alginate are cross-linked with polyvinyl alcohol (PVA) using calcium chloride (CaCl₂) (Inda, et al., 2018) to increase the mechanical strength of the pellet. Polyvinyl alcohol is a synthetic biopolymer that has biocompatibility, high elasticity and mechanical strength properties that can stabilize alginate (Xiao, et al., 2019). Banana peel activated carbon (BPAC), PVA and alginate are materials that are environmentally friendly materials. Furthermore, PVA/Alg pellet biopolymer impregnated with BPAC will be further crosslinked with glutaraldehyde (GA) (Komatsu, et al., 2015) by considering the results of Aprilia's research (2021) that the



amount of banana peels, size 60 mesh, impregnated into the PVA/Alg pellet biopolymer affected the mechanical strength of the material wall. Glutaraldehyde (GA) has unique characteristics so that it is one of the most effective protein crosslinking agents. In addition, GA has aldehyde groups which are highly reactive and can form a covalent bonds with functional groups such as hydroxyl, phenol, amine, thiol, and imidazole.

This research aims to synthesize PVA/Alg/GA pellet biopolymer containing BPAC, characterisation of pellet biopolymer and also the adsorption ability of pellet as an adsorbent in copper (II) ion adsorption.

2. MATERIALS AND METHOD

2.1 Materials

The materials used in this research were banana peel waste, distilled water, ammonium sulfate, PVA, alginate, glutaraldehyde, ZnCl₂, 0.1 M KMnO₄, 0.1 M HCl, NaOH, H₂SO₄, 10 wt% CaCl₂, CuSO₄ · 5H₂O, pH 6.8 buffer, and whattman 41 filter paper.

2.2 Methods

2.2.1 Preparation of Banana Peel Activated Carbon (BPAC)

Rippen banana peel (*Musa paradisiaca*) (yellow) were washed with water until clean, then cut into small pieces, then dried. The dried banana peel was carbonized in furnace and activated using activator ZnCl₂ and KMnO₄.

2.2.2 Preparation of PVA/Alg/GA Pellet Biopolymer Impregnated with BPAC [8]

Various mass of BPAC with 0 ; 0.5 and 1% were added into a solution containing PVA, alginate and distilled water, and stirred until homogen. The mixture was dropped into a CaCl₂ solution and allowed to solidify and formed a pellet. The PVA/Alg pellet biopolymer the immersed into glutaraldehyde solution. The obtained PVA/Alg/GA pellet biopolymer containing BPAC was rinsed using distilled water until the pH was neutral and soaked in distilled water until used.

2.2.3 Morphological Observation of PVA/Alg/GA Pellet Biopolymer Impregnated with BPAC

The morphology of pellet biopolymer was observed using a Scanning Electron Microscope (SEM).

2.2.4 Mechanical Strength of PVA/Alg/GA Biopolymer Pellets

The mechanical strength of PVA/Alg/GA pellet biopolymer was measured by the Hydraulic Impact Resistance method. The retention rate of undamaged beads is calculated by the equation:

$$\text{Damage Ratio Rate} = \frac{N_t}{N_o} \times 100\% \quad (1)$$

2.2.5 Extraction of Heavy Metal Ions using PVA/Alg/GA Biopolymer Pellets [8]

An amount of 0,2 g of pellet biopolymer was added into the 30 mL copper (II) solution, shaking for 24h and measured using AAS. The amount of copper adsorbed into the pellet biopolymer was calculated using equation (2).

$$\text{Adsorption Efficiency} = \frac{C_{Cu,ini} - C_{Cu,aq}}{C_{Cu,ini}} \times 100\% \quad (2)$$

where C_{Cu,ini} is the initial concentration of copper(II) ions in aqueous solution and C_{Cu,aq} is the concentration of copper(II) ions after extraction in aqueous solution.

3. REGIONAL GEOLOGY OF RESEARCH AREA

3.1 Preparation of Banana Peel Activated Carbon (BPAC)

Banana peel activated carbon was successfully prepared. The BPAC was then activated using activator ZnCl₂ and KMnO₄ and analysis using Scanning Electron Microscope (SEM). The SEM image shows that the BPAC has many pore on the surface area of activated carbon after activated using activator.

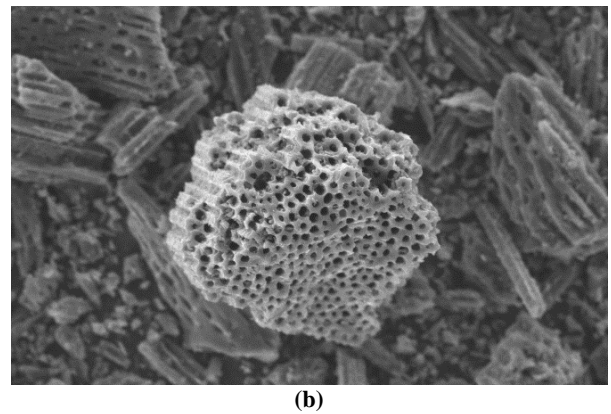


Figure 1 (a) BPAC (b) SEM Image of BPAC

3.2 Preparation of Pellet biopolymer PVA/Alg/GA Impregnated with BPAC

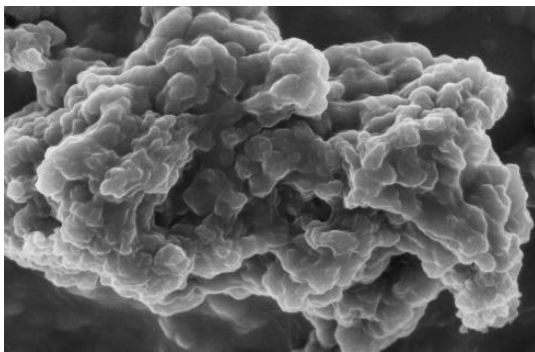
Preparation of PVA/Alg/GA pellet biopolymer impregnated with BPAC has been successfully carried out. The result shows that the pellets have a round shape, springy texture, and water content presence inside the pellet. Pellet biopolymer without BPAC has a white gel-like bead (Figure 2 (i)), pellet with 0.5 g of BPAC was dark gray (Figure 2 (ii)), and pellet with 1 g of BPAC was light gray (Figure 2 (iii)). The discoloration of pellet biopolymer is caused by the different color between BPAC and pellet. Therefore, when the BPAC impregnated into the pellet, the discoloration occurred from white to light and dark grey for 1 g and 0.5 gram of BAPC, respectively.



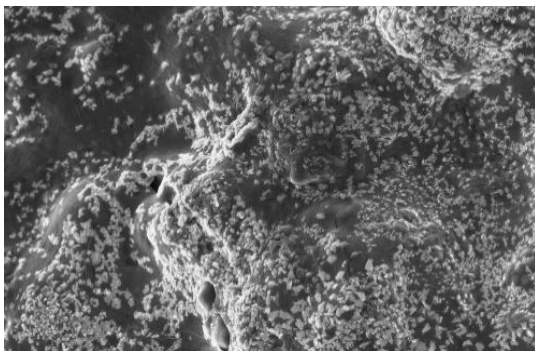
Figure 2. (i) PVA/Alg/GA pellet biopolymer without BPAC; (ii) PVA/Alg/GA with 0.5 g BPAC ; (iii) PVA/Alg/GA with 1 g BPAC

3.3 Morphological Observation of PVA/Alg/GA Pellet Biopolymer Impregnated with BPAC

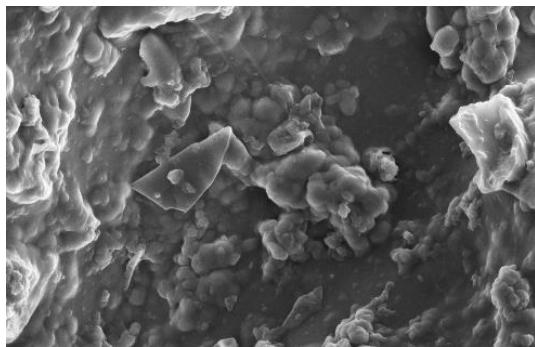
Morphological observation of pellet biopolymer PVA/ Alg/GA impregnated with BPAC was carried out using a Scanning Electron Microscope (SEM). The SEM images can be seen in Figure 3.



(a)



(b)



(c)

Figure 3. (a) Pellet biopolymer without BPAC, (b) pellet biopolymer with 0.5 g BPAC, (c) pellet biopolymer with 1 g BPAC

The SEM images show that the pellet biopolymer without BPAC has a grinding surface and pore. Whereas pellet biopolymer with 0.5 g of BPAC has a dense surface area, BPAC existed on the surface of the pellet and also a crack on the surface area. BPAC on the surface area of pellet found to be mostly have a square shape and spread out through the surface area of pellet and seen to be attached on the surface area of the pellet. Furthermore, pellet biopolymer with 1 g of BPAC found to have a dense surface area, grinding on the surface area and no BPAC presence on the surface area of the pellet. It can be considered that almost all of the BPAC have not attached on the surface area of pellet but have been coated into pellet biopolymer. The pellet biopolymer with 0.5 g of BPAC has a smoother surface area than pellet with 1 g of BPAC.

3.4 Mechanical Strength of PVA/Alg/GA Biopolymer Pellets

Mechanical strength using the Hydraulic Impact Resistance shows that the amount of BPAC impregnated into pellet biopolymer affected the mechanical strength of pellet biopolymer. Pellet biopolymer with 1 g of BPAC activated using $ZnCl_2$ have a better mechanical strength than pellet biopolymer with 0.5 g of BPAC activated using $ZnCl_2$ with the stability level of 94%. Whereas pellet biopolymer with 0.5 g of BPAC activated with $KMnO_4$ show a better mechanical strength than pellet biopolymer containing 1 g of BPAC activated with $KMnO_4$ with stability level of 98%. This is due to the $KMnO_4$ in acidic solutions such as HCl and glutaraldehyde will act as a strong oxidizing agent, where MnO^- will react with H^+ , form a OH^- and release into the aqueous solution, and form a Mn^{2+} . In neutral solutions, the oxidation of potassium is secondary, and the resulting reduction product is manganese dioxide. Meanwhile, in alkaline solution, the oxidation of potassium permanganate is weak because oxygen atoms do not easily to release, so they are reduced to manganese acid radical ions (Stastn, 2017).

3.5 Extraction of Heavy Metal Ions using PVA/Alg/GA Biopolymer Pellets [8]

The pellet biopolymer containing BPAC can be used as an adsorbent for copper (II) ion. The adsorption efficiency of copper (II) ion using pellet biopolymer containing BPAC is approximately 80% where 3.03 ppm for pellet biopolymer containing BPAC activated using $ZnCl_2$ and 3.675 ppm for pellet biopolymer containing BPAC activated using $KMnO_4$. These data indicate that PVA/Alg/GA pellet biopolymer containing BPAC can be recommended as an alternative

adsorbent in the field of advanced materials to overcome environmental pollution caused by copper (II) metal ions.

4. CONCLUSION

Pellet biopolymer PVA/Alg/GA containing BPAC show a have a round shape, springy texture, and water content presence inside the pellet. Pellet biopolymer impregnated with ZnCl₂ and KMnO₄, activated banana peel and activated carbon (BPAC) can be used as an adsorbent in adsorbing copper (II) metal ion with adsorption efficiency is approximately 80%.

ACKNOWLEDGMENTS

This research was supported by funds from the Directorate of Learning and Student Affairs as the activity organizer, so the authors would like to thank you for this assistance, as well as the support for the independent learning campus and Tadulako University who helped and provided direction during the PKM implementation.

REFERENCES

- [1] Ammar Staind. 2014. Waste processing. Jakarta.
- [2] Aprilia., N.F. 2021. Production of PVA/Na-Alginate Polymer Particles Containing Banana Peel (*Musa paradisiaca* L.) as Cu²⁺ Ion Biosorbent. Essay. Faculty of Mathematics and Natural Sciences Tadulako University, Palu.
- [3] Central Bureau of Statistics. 2020. Production of Fruit Plants. URL: <https://www.bps.go.id/indicator/55/62/1/production-tanaman-fruits.html>. Retrieved March 5, 2022. Du, Z., Liu, F., Xiao, C., Dan, Y., & Jiang, L., 2021, Fabrication of poly (vinyl alcohol)/sodium alginate hydrogel beads and its application in photo-Fenton degradation of tetracycline, *J. Mater. Sci.*, 56(1): 913-926.
- [4] El Hankari, S., Bousmina, M. and El Kadib, A., 2019. Biopolymer@ metal-organic framework hybrid materials: a critical survey. *Progress in Materials Science*, 106, p.100579.
- [5] Fertahi, S., Ilsouk, M., Zeroual, Y., Oukarroum, A. and Barakat, A., 2021. Recent trends in organic coating based on biopolymers and biomass for controlled and slow release fertilizers. *Journal of controlled release*, 330, pp.341-361.
- [6] Hidayah, N, Deviyani, E, Wicakso, D.R. 2012. Adsorption of Iron (Fe) in the Barito River using adsorbents from banana stems. *Conversion*. 1(1):19-25.
- [7] Inbaraj, B.S., Wang, J.S., Lu, J.F., Siao, F.Y. and Chen, B.H., 2009. Adsorption of toxic mercury (II) by an extracellular biopolymer poly (γ -glutamic acid). *Bioresource Technology*, 100(1), pp.200-207.
- [8] Inda, N. I., Fukumaru, M., Sana, T., Kiyoyama, S., Takei, T., Yoshida, M., Nakajima, A. and Shiomori, K. 2018. A Kinetic Study of Copper(II) Extraction using LIX84-I Impregnated Polymeric Particles with Different Structures. *SERDJ*. 25(1): 23-36.
- [9] Islamiyah, S.N., & T. Koestiari. 2014. Analysis of Copper(II) Metal Content in Kenjeran Seawater. National Proceedings of Chemistry, ISBN: 978-602-0951-00-3
- [10] Kalyani, S., Priya, J.A., Rao, P.S. and Krishnaiah, A.J.S.S., 2005. Removal of copper and nickel from aqueous solutions using chitosan coated on perlite as biosorbent. *Separation science and technology*, 40(7), pp.1483-1495.
- [11] Komatsu, S., Kiyoyama, S., Takei, T., Yoshida, M., Shiomori, K. 2015. Extraction Equilibrium of Co(II) with Microcapsules of Cross-linked Gel of Poly (vinyl alcohol)/Alginic Acid Encapsulating Dispersed Droplets of 2-ethylhexyl Phosphonic Acid 2-ethylhexyl Ester. *環境資源工学*. 62: 56-62.
- [12] Oyewo, O. A., Onyango, M. S. and Wolkersdorfer, C. 2017. Lanthanides Removal from Mine Water using Banana Peels Nanosorbent. *int. J. Environ. sci. Technol.* 15(6): 1256-1274.
- [13] Pezoti Jr., O., Cazetta, A.L., Souza, I.P.A.F., Bedin, K.C., Martins, A.C., Silva, T.L and Almada, V.C. 2014. Adsorption studies of methylene blue onto ZnCl₂-activated carbon produced from buriti shells (*Mauritia flexuosa* L.), *Journal of Industrial and Engineering Chemistry*, 20(6):4401-4407.
- [14] Rodriguez, M.S., Zalba, M.S., Debbaudt, A.L. and Agullo, E., 2006. New chitosan-calcium pectinate pellets and their adsorption capacity. *Colloid and Polymer Science*, 285(1), pp.119-124.
- [15] Saeidi, N. and Lotfollahi, M. N. 2015. Effects of powder activated carbon particle size on adsorption capacity and mechanical properties of the semi activated carbon fiber. *Fibers and Polymers*. 16(3): 543-549.
- [16] Singha, A.S. and Guleria, A., 2014. Use of low cost cellulosic biopolymer based adsorbent for the removal of toxic metal ions from the aqueous solution. *Separation Science and Technology*, 49(16), pp.2557-2567.
- [17] Sires, J. (2017). A review of potential zinc and copper pollution sources in the kenai river watershed. Get to the Watershed Forum. Alaska, USA: Department of Environmental Conservation.
- [18] Solgi, M., G. Tabil, L. and D. Wilson, L., 2020. Modified biopolymer adsorbents for column treatment of sulfate species in saline aquifers. *Materials*, 13(10), p.2408.
- [19] Stastn, M., J. Tolasz, V. Stengl, J. Henych, D. Zsayazka. 2017. Gravene Oxide/MnO₂ Nano Composite as a Destructive Adsorbent of Nerve Agent Simulants in Aqueous Media, *Appl. Surfing. sci.* 412 19-28.
- [20] Suliestyah, D. Ariani, Astuti. 2021. Optimization of ZnCl₂ activator in producing activated carbon from coal and testing activated carbon as an adsorbent. *Journal of Research and Scientific Work Trisakti University Research Institute*. 6(2):191-201.
- [21] Vijaya, Y., Popuri, S.R., Boddu, V.M. and Krishnaiah, A., 2008. Modified chitosan and calcium alginate biopolymer sorbents for removal of nickel (II) through adsorption. *Carbohydrate polymers*, 72(2), pp.261-271.
- [22] Vitali, L., Justi, K.C., Laranjeira, M. and Fávere, V.T., 2006. Impregnation of chelating agent 3, 3-bis-N, N bis-(carboxymethyl) aminomethyl-o-cresolsulfonephthalein in biopolymer chitosan: adsorption equilibrium of Cu (II) in aqueous medium. *Polímeros*, 16, pp.116-122.
- [23] Xiao, Z., Zhang, L., Wu, L. and Chen, D. 2019. Adsorptive Removal of Cu(II) from Aqueous Solutions using a Novel Macroporous Bead Adsorbent Based on Poly(vinyl alcohol) /Sodium Alginate/KMnO₄ Modified Biochar. *J.Taiwan Inst. Chem. Eng.* 102: 110-117.