Comparative study of methylene blue adsorption using alkali-activated pumice from Bali and Banten

V Prajaputra¹, Z Abidin², S Budiarti³, D T Suryaningtyas⁴ and N Isnaini⁵

¹ Doctoral Student of Natural Resources and Environmental Management Study Program, IPB University, Bogor, 16144, Indonesia.
² Department of Chemistry, IPB University, Bogor, 16680, Indonesia.
³ Department of Biology, IPB University, Bogor, 16680, Indonesia.
⁴ Department of Soil Sciences and Land Resources, IPB University, Bogor, 16680, Indonesia.
⁵ Atsiri Research Center, Universitas Syiah Kuala, Banda Aceh, 23111, Indonesia.

E-mail: abidinzed@apps.ipb.ac.id, vicky_prajaputra@apps.ipb.ac.id

Abstract. This study presents the comparison of methylene blue (MB) adsorption using alkali-activated pumice from Bali (A-P1) and Banten (A-P2). Pumice samples were activated under alkaline solution and followed by simple hydrothermal treatment in a polypropylene bottle at 100 °C for 24 hours. The X-ray diffraction (XRD) patterns showed that both treated pumices have different peak characteristics, where only A-P1 was dominated by the mineral phase of GIS-NaP1 zeolite. The change of amorphous to zeolite phases increased negative sides and caused A-P1 to have a higher adsorption capacity than A-P2. Based on the adsorption data of A-P1 and A-P2, the Langmuir isotherm model shows a better fit with high correlation values ($R^2$) compared to the Freundlich model. This means the interaction between the treated pumice and MB followed the assumption of monolayer coverage on homogeneous surfaces, in which the maximum values of MB adsorption were found to be 51.546 mg/g for A-P1 and 27.027 mg/g for A-P2. In addition, A-P1 and A-P2 were also potentially used as heterogeneous catalysts for MB degradation through Fenton-like process due to the presence of iron oxide contents.

1. Introduction

Methylthioninium chloride ($C_{16}H_{18}ClN_3S$), known as methylene blue (MB), has been described as the first synthetic drug used in clinical therapy for the treatment of malaria since more than a century ago [1]. It was then replaced by chloroquine (CQ) and other synthetic drugs from its derivatives because the use of MB is confirmed having several toxic effects in high doses (>2 mg/kg) and causing bluish discoloration of the sclera (the whites of the eyes) for patients [2]. In order to combat CQ resistance, the potential structure of MB as an antimalarial agent was revisited and further investigated by experts [3-5]. Several clinical trials in vitro and in vivo using combination of MB and QC to treat malaria in Africa have been reported [6, 7]. Apart from being an antimalarial, MB is used as a fungicide for fish infection and also as coloring agents in several industries with a large scale such as textiles, paper, ink, and plastics [8, 9]. The high use of MB certainly contributes to the contamination of these compounds in water and causes environmental damage due to its various negative impacts and difficult to degrade naturally.

Adsorption is one of the most frequent methods used to eliminate organic pollutants from water due to its high selectivity, inexpensive, and easy to apply on a large scale without requiring a lot of reagents.
and high energy consumption [10, 11]. Many studies have reported the use of biomass-based activated carbon as adsorbent because of its high effectiveness to eliminate various types of pollutants in water, both organic and inorganic [12, 13]. A very intriguing study by Bayomie et al. [14] found that the activated carbon (AC) prepared from fava bean peel waste has an adsorption capacity of 140 mg/g for methylene blue removal. Nevertheless, the price of AC is quite expensive because it is produced from the combustion of organic materials (wood, coconut shells, and other biomass) at high temperatures [15, 16]. Therefore, various attempts are continuously being made by experts to develop more efficient and inexpensive adsorbents from natural sources such as volcanic ash [17], zeolite [18], kaolin [19], and pumice [20].

Indonesia is surrounded by many volcanoes starting from the islands of Sumatra, Java, Sulawesi, Maluku, Bali, and Nusa Tenggara, so it is well-known as a country located in the Pacific Ring of Fire region. The eruptive activity of volcanoes produces various volcanic materials, one of which is pumice [21]. Due to the frequent volcanic eruptions in Indonesia, the availability of pumice is abundant, especially in the area around volcanoes. Pumices are formed from the process of freezing lava rapidly. This rock has a low density (less than 1 g/cm3) because the average size of its porosity can reach 90% [22]. In addition, pumices are also composed of aluminosilicate minerals whose surface charge is highly dependent on environmental pH conditions [23]. A very intriguing study by Hasanah et al. [20] reported the use of pumice from Lombok and Kediri as a potential adsorbent for lead (Pb) removal. The results showed that the adsorption capacity increased after being activated with an alkaline solution. In this study, the adsorption ability of pumices obtained from Bali and Banten will also be enhanced by chemical activation using alkaline media, which is then followed by hydrothermal treatment. This research objective is to compare the ability of alkali-activated pumice from Bali and Banten for MB removal in aqueous solution.

2. Experimental

2.1. Materials

Pumice samples were obtained from two regions in Indonesia (Bali and Banten) with different colors (figure 1). The collected samples were then dried, crushed, and filtered using a sieve of 100 mesh to reduce the particle size. Methylene blue with a purity percentage of 98.5% was purchased from Kanto Chemical Co., Inc. Sodium hydroxide (NaOH) and hydrogen peroxide (H2O2) of analytical reagent grade were purchased from Merck (Darmstadt, Germany). A stock solution of MB (500 mg/L) was prepared using distilled water, which was further diluted into several concentrations.

2.2. Preparation and characterization materials

Alkali-activated pumice was prepared through a simple hydrothermal treatment without further purification. For the first step, pumice powder as much as 10 g was weighed and mixed with 80 mL of sodium hydroxide solution (3 mol/L) and stirred in a sealed polypropylene bottle for 30 minutes at room temperature (28 °C). The mixture was heated using a drying oven at 100 °C for 24 hours. Afterward, the
solid phase was separated from the supernatant and rinsed several times with distilled water until the pH near to be 7. It was then dried (at 100°C for 12 hours), crushed, and filtered again using a sieve of 100 mesh. The final solid obtained was called alkali-activated pumice, which was further characterized by using XRD (Bruker D8 model, USA) with Cu Kα radiation at a voltage of 40 kV and current of 30 mA. The instrument was set at scanning rate of 2°/min (2 theta degree from 5–50°).

2.3. Adsorption studies
The comparative study of MB adsorption using A-P1 and A-P2 was performed by shaking 0.01 g of adsorbents within 5 mL of MB solution in different initial concentrations (25, 50, 75, 100, 150, 200, and 300 mg/L) for a day with assumption that the adsorption equilibrium was achieved. After equilibrium state, each solution was separated from adsorbents and the final MB concentration was measured using a visible spectrophotometer (Biochrom Libra S11) at 665 nm as the maximum wavelength obtained in this study. Based on equation 1, the adsorption capacity (qₑ, in mg/g) was calculated.

\[
qₑ = \frac{(C₀ - Cₑ)}{m} \times V
\]  

(1)

Where \(C₀\), \(Cₑ\), \(m\), and \(V\) are initial MB concentration (mg/L), MB concentration at equilibrium (mg/L), \(m\) is mass of adsorbent (g), and volume of MB (L), respectively. The collected data was then analyzed by two isotherm models, namely Langmuir and Freundlich. Both of these isotherm models were used to study the adsorption behaviour of MB using activated pumice and also to determine the maximum adsorption capacity. The linear forms of Langmuir and Freundlich models were expressed in equations 3 and 4.

\[
\frac{Cₑ}{qₑ} = \frac{1}{bq_{max}} + \frac{Cₑ}{q_{max}}
\]  

(2)

Langmuir:

\[
\log qₑ = \log K_f + \frac{1}{n_f} \log Cₑ
\]  

(3)

Freundlich:

Where \(q_{max}\), \(b\), \(K_f\), and \(n_f\) refer to the maximum value of adsorption capacity (mg/g), the Langmuir constant (L/mg), the Freundlich constant (L/g), and the adsorption intensity (g/L), respectively.

2.4. Degradation of MB
The ability of adsorbents to degrade adsorbed MB was tested within several centrifuge tubes. For the qualitative test, each adsorbent as much as 0.01 g was mixed with 5 mL (100 mg/L) of MB for 24 hours. After that, the mixture was separated and two drops of hydrogen peroxide (12.8 mol/L) were added to the adsorbent. For the quantitative test, the same procedure was also carried out as before without separation by adding 0.1 mL of hydrogen peroxide to the mixture. The final concentration after degradation for 24 hours (\(C_t\)) was measured using a visible spectrophotometer to calculate the percentage of MB degradation (\% Deg).

\[
\% \text{Deg} = \left(\frac{Cₑ - C_t}{Cₑ}\right) \times 100
\]  

(4)
3. Result and discussion

3.1. Characterization of samples

Pumice chemical compositions were obtained from X-ray fluorescence (XRF) analysis. The results indicate that pumice main components are composed of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$. Based on the XRD pattern, pumice from Bali contains a high amorphous silica phases, especially at $2\theta = 15-30^\circ$, which similar to the pumice from Lombok [25]. However, several studies have also reported that pumice is sometimes dominated by crystalline minerals, such as forsterite, pyroxene, orthoclase, anorthite, hematite, and apatite [26-28].

In this study, XRD patterns of both alkali-activated pumices are compared and displayed in Figure 2. As seen, several peaks were formed in the A-P1 at $2\theta = 12.48^\circ$, 17.70$^\circ$, 21.65$^\circ$, 28.07$^\circ$, 33.39$^\circ$, 38.02$^\circ$, and 46.02$^\circ$. The mentioned peaks correspond to the crystalline phases of GIS-NaP1 zeolite with similar characteristics to the reference (JCPDS 01-071-0962). This condition may be due to the present of high amorphous silica and aluminum oxides on the pumice sample from Bali (P1) as precursors in the formation of zeolite frameworks. Before the hydrothermal treatment, the solution was obtained at pH=12. As reported before, the pH value plays an important factor in the growth of zeolite crystals because OH$^-$ ions act as mineralization agents to dissolve Si and Al oxides [29]. These dissolved precursors contain ligands that can condense with each other and are considered to be the first step in zeolite crystal formation (nucleation) by rearranging their structures to form T-O-T polymer chains (T = Si or Al). In general, the rate of zeolite crystal growth increases with increasing the alkaline concentration and will continue until there is no more dissolved amorphous gel phase. However, the polycondensation was also inhibited in the case of high alkaline concentrations. According to Ayele et al. [30], the use of 3.0 mol/L NaOH concentration on the synthesis of zeolites produced the best crystallinity.

![Figure 2. XRD Patterns of (a) A-P1 and (b) A-P2.](image)

The hydrothermal process increased the rate of nucleation and caused the crystal arrangement more regular. On the otherhand, the length of hydrothermal time can also affect the phase of zeolite crystal formation, in which the most thermodynamically unfavorable phase will crystallize first and be replaced
in sequence with a more stable phase (e.g. amorphous phase → faujasite → NaP1) [31]. The type of zeolite formed depends on the Si/Al ratio. According to Löwenstein's rule, the minimum limit for the Si/Al lattice ratio in zeolite synthesis is 1 because the formation of Al-O-Al bonds is avoided. The previous study reported that zeolite Na-P1 had the ratio value of Si/Al in the range of 1.10-2.30 with cation exchange capacity (CEC) values from 193 to 479 cmol/kg, depending on the pH of the zeolite [32].

In contrast to A-P1, the mineral phases found in A-P2 are more varied, such as forsterite, anorthite, leucite, apatite, orthoclase, and some of zeolite minerals (mordenit and NaP1). Although the mineral phase characterization of P2 was not performed, it can be assumed that the sample has several crystalline minerals (not just amorphous minerals). This condition certainly affected the formation of zeolite crystals as a consequence of less amorphous aluminosilicate dissolution, so that A-P2 only produced a small part of the zeolite phase depending on the amount of aluminosilicate dissolution. In addition, the crystalline minerals present in P2 sample may also be present in A-P2.

3.2. Equilibrium adsorption and isotherm studies

Figure 3 shows the adsorption capacity of pumice before and after the treatment process. As seen, the adsorption ability of both treated pumices increased greatly after being activated under alkaline media, where A-P1 exhibited a high adsorption capacity compared to A-P2. The adsorption capacity of A-P1 increases from 13.28–48.83 mg/g in the range concentration of 25–150 mg/L and tends to be constant at 150–300 mg/L. This means the equilibrium state was found at MB concentration of 150 mg/L. On the other hand, the ability of A-P2 to uptake MB also increased from 12.89–24.55 mg/g at 25–75 mg/L, but the adsorption capacity tends to be constant at concentrations above 75 mg/L. The increase in adsorption capacity that occurred in both alkaline-activated pumice samples was caused by the formation of new silanol (Si-OH) groups, thereby increasing the negative charge on their surface and increasing their ability to adsorb MB (cationic compounds). However, under certain conditions, the adsorbents will reach a saturation state because of the negative charge limitation on their surfaces. According to Guler and Sarioglu [33], if pumice is activated in an acidic media, the negative charge on the pumice stone will decrease.

Figure 3. The adsorption of MB using A-P1 and A-P2.

Adsorption isotherm provides useful information regarding the maximum amount of adsorbate that can be absorbed by the adsorbent at constant temperature. In this study, the relationship between alkali-activated pumice and MB was studied using Langmuir and Freundlich isotherm models. Figure 4 shows the linearity of Langmuir and Freundlich isotherms using A-P1 and A-P2. The Langmuir isotherm for both activated pumice stones has a higher correlation coefficient (R²) value than Freundlich isotherm. This indicates that the interaction between adsorbent (A-P1 or A-P2) and adsorbate (MB) follows the
assumption of homogeneous adsorption with monolayer coverage, where the maximum adsorption capacities of A-P1 and A-P2 were found to be 51.546 mg/g and 27.027 mg/g, respectively. However, the maximum uptake capacities of initial samples were only about 11.223 mg/g for P1 and 10.427 mg/g for P2. Table 1 shows the values of several Langmuir and Freundlich isotherm parameters. The b value, which was obtained from the result of plotting between Ce/qe and Ce, indicated the strength of the adsorbate binding to the adsorbent surface. The high value of b on A-P1 (0.290 L/mg) means that the binding energy is stronger than that of A-P2 (0.268 L/mg).

3.3. Degradation of MB

After the equilibrium state, each adsorbent (A-P1 and A-P2) was separated from MB solution and added two drops of hydrogen peroxide to determine their potential for degrading MB adsorbed. The qualitative degradation test results showed that the two activated pumice samples have higher degradation abilities than the initial pumice samples. It was evidenced by the loss of the blue color absorbed on the adsorbent surfaces (Figure 5). Increasing degradation ability of activated pumice samples may be due to the formation of other iron oxide deposits during the hydrothermal process under alkaline solution, which in turn enhanced the MB degradation process through the reaction below.

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow [\text{Fe}^{III}\text{OOH}]^{2+} + \text{H}^+ & (5) \\
[\text{Fe}^{III}\text{OOH}]^{2+} & \rightarrow \text{Fe}^{2+} + \cdot \text{OOH} & (6) \\
[\text{Fe}^{III}\text{OOH}]^{2+} & \rightarrow [\text{Fe}^{IV}\text{O}]^{2+} + \cdot \text{OH} & (7)
\end{align*}
\]

Iron oxide contents play a role as Fe$^{3+}$ ion sources to form [Fe$^{III}$OOH]$^{2+}$ intermediate as the first step reaction in the presence of H$_2$O$_2$. The intermediate might be possible to bond with organic compounds or break up at the Fe-O bond to generate Fe$^{2+}$ and hydroperoxyl radical (•OOH). It might be also break up at the O-O bond by generating the ferryl ion ([Fe$^{IV}$O]$^{2+}$) and hydroxyl radical (•OH). The hydroxyl radicals as a quite reactive species then preferentially attack the benzene ring of MB to form the final
mineralization products. Because A-P1 and A-P2 showed their ability as heterogeneous Fenton-like catalyst, the quantitative degradation test was also carried out by measuring the MB concentration before (at the equilibrium state) and after the degradation process for 24 hours. The results indicated that A-P1 and A-P2 were able to degrade MB with the percentage of 99.94% and 99.71%, respectively. The occurrence of MB degradation was indicated by the loss of the MB absorption peak at 600-700 nm (at the time of adsorption equilibrium), which was measured using a visible spectrophotometer (Figure 5).

4. Conclusion
The abilities of pumice from Bali and Banten, which was activated under alkaline media and followed by the hydrothermal treatment, have been investigated in this study. XRD patterns of both treated pumice showed different mineral phases, where A-P1 was mostly dominated by the phase of zeolite NaP1. The maximum adsorption capacities of A-P1 and A-P2 were found to be 51.546 mg/g and 27.027 mg/g, respectively. Adsorption process was better fitted to the Langmuir isotherm model with a high correlation value \( R^2 \) compared to the Freundlich isotherm model. This means the relationship between adsorbents and adsorbates followed the assumption of monolayer adsorption on homogenous surfaces. Moreover, A-P1 and A-P2 also showed their catalytic properties to degrade MB with high degradation ability through the Fenton-like reaction.

Acknowledgements
The authors would like to thank the Ministry of Research, Technology and Higher Education (RISTEKDIKTI) of the Republic of Indonesia for financial support through PMDSU scholarship and also to the Teaching Laboratory of IPB University for facilitating this research.
References

[1] Howland R H 2016 J. Psychosoc. Nurs. Ment. Health Serv. 54 21
[2] Ginimuge P R and Jyothi S 2010 J. Anaesthesiol. Clin. Pharmacol. 26 517
[3] Anh C X, Chavechich M, Birrell G W, Van Breda K, Travers T, Rowcliffe K, Lord A R, Shanks G D and Edstein M D 2020 Antimicrob. Agents Chemother. 64 e01441
[4] Pascual A, Henry S, Briolant S, Charras S, Baret E, Amalvic R, des Etages E H, Feraud M, Rogier C and Pradines B 2011 Antimicrob. Agents Chemother. 55 2472
[5] Dormoi J, Pascual A, Briolant S, Amalvic R, Charras S, Baret E, des Etages E H, Feraud M and Pradines B 2012 Antimicrob. Agents Chemother. 56 3467
[6] Lu G, Nagbanshi M, Goldau N, Jorge M M, Meissner P, Jahn A, Mockenhaupt F P and Mueller O 2018 J. Appl. Phys. 16 59
[7] Garavito G, Bertani S, Quiliano M, Valentín A, Aldana I and Deharo E 2012 Mem. Inst. Oswaldo Cruz 107 820
[8] Jawad A H, Rashid R A, Mahmuod R M, Ishak M A M, Kasim N N and Ismail K 2016 Desalination Water Treat. 57 8839
[9] Wang Y, Huang X, Lv X, Sun J, Zheng R and Hu K 2020 J. Ocean Univ. China 19 653
[10] Kou X, Ma B, Zhang R, Cai M, Huang Y and Yang Y 2020 RSC Adv. 10 20338
[11] Sadegh H, Mazloumbilandi M and Chahardouri M 2017 Handbook of ecomaterial 1–33
[12] Kavand M, Eslami P and Razeh L 2020 J. Water Process. Eng. 34 101151
[13] Allgayer R, Yousefi N and Tufenkji 2020 Environ. Sci. Nano. 7 2669
[14] Bayomie O S, Kandeel H, Shoeib T, Yang H, Youssef N and El-Sayed M M 2020 Sci. Rep. 10 1
[15] Park H -S, Koduru J R, Choo K -H and Lee B 2015 J. Hazard. Mater. 286 315
[16] Lee S -H and Kwon D -Y 2020 Desalination Water Treat. 57 8026
[17] Cáceres-Jensen L, Rodríguez-Beccerra J, Parra-Rivero J, Escudey M, Barrientos L and Castro-Castillo V 2013 J. Hazard. Mater. 261 602
[18] Shaban M, Abu Khadra M R, Nasief F M and Abd El-Salam H 2017 Water Air Soil Pollut. 228 450
[19] Gao W, Zhao S, Wu H, Deligeer W and Asuha S 2016 Appl. Clay Sci. 126 98
[20] Hasanah F, Anwar S, Hartono A and Sudadi U 2019 ST-JSSA 16 203
[21] Jutzeler M, Marsh R, Carey R J, White J D, Talling P J and Karlstrom L 2014 Nat. Commun. 5 1
[22] Ismail A, El-Shafey O, Amr M and El-Maghraby M 2014 Int. Sch. Res. Notices. 2014 1
[23] Ersoy B, Sarisik A, Dikmen S and Sarisik G 2010 Powder Technol. 197 129
[24] Putri M and Darminto D 2018 International Basic Science Conference 107–110
[25] Prajarputra V, Abidin Z, Widiata M, Suryaningtyas D T and Rizal H 2019 IOP Conf. Ser. Earth Environ. Sci. 399 012014
[26] Mourhly A, Khachani M, Hamidi A E, Kacimi M, Halim M and Arsalane S 2015 Nanomater. Nanotechnol. 5 35
[27] Samimi K, Kamali-Bernard S, Maghsoudi A A, Maghsoudi M and Siad H 2017 Constr. Build Mater. 151 292
[28] Mboya H A, King’ondu C K, Njau K N and Mrema A L 2017 Adv. Civ. Eng. 2017 1
[29] Wilińska I and Paceswka B 2019 J. Therm. Anal. Calorim. 138 3875
[30] Ayele L, Perez-pariente J, Chebude Y and Diaz I 2015 Microporous Mesoporous Mater 215 29
[31] Barrer R M 1982 Hydrothermal chemistry of zeolites Academic press
[32] Munthali M W, Elsheikh M A, Johan E and Matsue N 2014 Molecules 19 20468
[33] Guler U A and Sarioglu M 2014 J. Environ. Health Sci. Eng. 12 79