POTENTIAL USE OF ALKALINE-ACTIVATED INDONESIAN PUMICE POWDER AS LEAD ADSORBENT IN SOLUTION SYSTEM

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ABSTRACT

Pumice is a volcanic material that found abundant in Indonesia. Owing to its physicochemical characteristics it can be utilized as a low-cost natural adsorbent for cationic contaminants. This study aimed to assess the performances of adsorbents prepared from NaOH-activated powder of Lombok and Kediri pumices for lead removal in solution systems based on their maximum adsorption capacity and removal efficiency parameters. The adsorption tests were done in batch experimentation using pumice powder of 74 μm particle size activated with 0.5, 1, and 2 M NaOH and lead solutions with initial concentrations of 0-260 mg.L-1. The most favorable NaOH activation concentration for both pumices was 0.5 M which resulted from Lombok pumice prepared-adsorbent with Pb maximum adsorption capacity based on linearized conventional and rearranged Langmuir isothermal adsorption models of 236.4 and 186.3 mg.g-1, while those of Kediri pumice were of 218.4 and 210.8 mg.g-1, respectively. The removal efficiency of both adsorbents were >80% at the initial Pb concentration of <100 mg.L-1 and around 50-80% at 100-260 mg.L-1. Both pumices are therefore considered potential to be utilized as an adsorbent for cationic contaminants in solution systems with reliable performances.

Keywords: Kediri pumice, Langmuir adsorption model, Lombok pumice, Natural adsorbent


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INTRODUCTION

Lead is one of the highly toxic heavy metal contaminants in the environment. Its contamination to the food chains can injure the fetal brain, kidneys, circulatory, and nervous systems, especially for children (Abas, Ismail, Kamal, & Izhar, 2013). Blacksmith Institute included lead as the top six environmental toxic threats (Pure Earth & Green Cross Switzerland, 2015). The sources of lead exposure to the environment include metal plating and finishing operation, wastes of battery industries, pigments and paints, factory chimneys, smelting of mine ores, fertilizers, and pesticides (Jaishankar, Tseten, Anbalagan, Mathew, & Beeregowda, 2014; UNEP, 2018). According to the DALY’s ranking for the worst polluting industries, based on contribution to the global burden disease, ULAB (used lead-acid battery) and lead
Environmental contaminations of Pb in Indonesia, among others, were reported by Paundanan, Riani, & Anwar (2015); Riza, Bambang, & Kismartini (2016); and Tjahjono & Suwarno (2018). Waters of Kartini Beach, Central Java contained Pb of 0.009 mg.L⁻¹ (Riza et al., 2016), while that of Palu Bay, Central Sulawesi was of 0.013-0.0392 mg.L⁻¹ (Paundanan et al., 2015), and that of the river of Demak Estuary, Central Java ranged from 0.6037 to 0.6647 mg.L⁻¹ (Tjahjono & Suwarno, 2018), all were surpassing the water quality standard set in the Environment Minister Decree, Government of Indonesia No 51 year 2004 (i.e. 0.008 mg.L⁻¹).

Treatment technologies to overcome heavy metal contamination in the environment have been widely developed, including precipitation, coagulation-flocculation, sedimentation, floatation, filtration, membrane processes, electrochemical techniques, biological processes, adsorption, and ion exchange, with varying levels of success. Adsorption is one of the most efficient strategies for the removal of various contaminants from aqueous solutions owing to a simple design, convenience, low cost, high efficiency, and wide adaptability (Foo & Hameed, 2010; Zhang et al., 2019). For a long term treatment of heavy metal removal, the adsorption process is considered as the most effective and economical approach (Abas et al., 2013).

The adsorption capacity of an adsorbent can be improved by applying two fundamental approaches, i.e. preparation of new adsorbent with excellent performance for contamination control and optimization of the adsorption conditions (Zhang et al., 2019). Çifçi & Meriç (2016) reported that pumice was a very attractive adsorbent of chromium (VI) from its maximum adsorption capacity that was higher than bentonite, clinoptilolite, and charcoal, and cost evaluation that was about 100 times cheaper than chitin, chitosan, and activated carbon.

This study is attempting to obtain adsorbents with higher lead adsorption capacity and removal efficiency as compared to several other adsorptive materials, including pumice, from other countries. The results of this study are expected to be beneficial for improving the utilization of Indonesian pumices, owing to their specific physicochemical characteristics and abundant reserves, as an excellent natural adsorbent for the removal of lead and other cationic contaminants from waters and wastewaters. This study aimed to assess the performances of adsorbent prepared from NaOH-activated powder of two Indonesian pumices for lead removal in solution system based on the maximum adsorption capacity and removal efficiency parameters by applying the conventional and rearranged linearized Langmuir isothermal adsorption models.

MATERIAL AND METHODS
This research was conducted from November 2018 to June 2019. The pumice raw materials were obtained from the eruption’s area of Mt. Rinjani and of Mt. Kelud at respectively Geres village, Labuhan Haji sub-district, East Lombok district, West Nusa Tenggara province, and Wonorejo Trisulo village, Plosoklaten sub-district, Kediri district, East Java province. The experiments were carried out at the Laboratory of Soil Chemistry and Fertility Division, Faculty of Agriculture, IPB University.
Preparation and activation of pumice powder as adsorbent

The materials were first ground and washed with running tap water to remove any impurities and rinsed with distilled water. Then, they were treated with 0.1 M HCl to dissolve acid-soluble impurities for further purification (Jonasi, Matina, & Guyo, 2017). After 24 h acid treatment, the materials were washed again with distilled water to remove excess acid until the pH of the washing water was equal to that of distilled water. The washed materials were oven-dried at 60 °C for 24 h to evaporate the remaining water. The dried materials were then milled and sieved to obtain pumice powder with the particle size of 200 mesh (74 μm).

Chemical modification of the pumice powder to prepare and improve its adsorption capacity as a cationic adsorbent was done by alkaline treatment in which 4 x 5 g pumice powder were dissolved each in 50 mL of 0 (control), 0.5, 1, and 2 M NaOH and agitated using end-to-end shaker at 175 rpm for 24 h at room temperature. The activated pumice powder was subsequently washed several times with distilled water to remove excess NaOH until pH of the washing water was equal to that of distilled water, and oven-dried at 105°C for 24 h to obtain solids for the batch experiment.

Adsorption test

The lead adsorption tests were carried out in batch experiments at 30 °C by adding 14 x 0.12 g of each adsorbents (activated-pumice powder, i.e. L0, L0.5, L1, L2, K0, K0.5, K1, and K2, where L designated for Lombok pumice; K for Kediri pumice; 0, 0.5, 1, and 2 for NaOH activation concentrations of 0 (natural pumice), 0.5, 1, and 2 M, respectively) to polyethylene bottles containing lead solutions prepared from Pb(NO₃)₂, 10 mL 0.01 M CaCl₂ as background electrolyte, and distilled water up to a final volume of 100 mL to get solutions with initial Pb concentrations ranging from 0 to 260 mg.L⁻¹ (0, 5, 10, 15, 20, 30, 40, 50, 60, 100, 140, 180, 220, and 260 mg.L⁻¹). The solutions were then agitated using end-to-end shaker at 150 rpm for 100 min to ensure that maximum adsorption at equilibrium state was achieved (Jonasi et al., 2017). The solutions were filtered and their pH and Pb concentrations were then respectively determined by using pH-meter and atomic absorption spectrophotometer (AAS). The working pH of the initial solution at equilibrium for Pb adsorption process on adsorbents prepared from Lombok pumice activated with 0, 0.5, 1, and 2 M NaOH were 6.5, 6.62, 6.61, and 6.54, while those from Kediri pumice were 6.17, 6.49, 6.38, and 6.2, respectively.

Data analysis

The maximum Pb adsorption capacity was calculated by using the linearized Langmuir isothermal adsorption model (Equation 1).

\[
\frac{C}{x/m} = \frac{1}{b} + \frac{1}{kbC}
\]  

[1]

where \( C \) = Pb concentration at equilibrium (mg.L⁻¹), \( x/m \) = amount of Pb adsorbed per unit mass of the adsorbent (mg.g⁻¹), \( b \) = maximum amount of adsorbate (Pb²⁺) that can be adsorbed as a complete monolayer by the adsorbent (mg.g⁻¹), and \( k \) = adsorption-desorption bonding energy for the adsorbate (Bohn, McNeal, & O’Connor, 2001; Silva-yumi, Escudey, Gacitua, & Pizarro, 2018). The Pb removal efficiency was determined using Equation 2.

Removal efficiency (\( \% \)) = \( \left( \frac{C_0 - C_f}{C_0} \right) \times 100 \)  

[2]

where \( C_0 \) = initial Pb concentration (mg.L⁻¹) and \( C_f \) = Pb concentration at equilibrium (mg.L⁻¹) (Ponce-Lira et al., 2017).
RESULTS

Lead adsorption isotherm shape and curvature

The adsorption reaction behavior can be interpreted by (1) identification of the adsorption isotherms shape and curvature, and (2) statistical modeling. The shape and curvature of lead adsorption isotherm (Figure 1) of the Lombok and Kediri adsorbents prepared from each respective alkaline-activated pumice powder by using the so-called conventional Langmuir model (Shukla, Matsue, Henmi, & Johan, 2011) resembled L-shape curves that indicate the solid adsorbent have a high affinity for the solute (Tan, 2011). The Langmuir isotherm curve can also be described mathematically, known as the rearranged Langmuir model, by applying the statistical modeling method (Essington, 2004; Sposito, 2008).

Lead maximum adsorption capacity based on conventional Langmuir model

Lead adsorption isotherm plots of the tested Lombok and Kediri adsorbents prepared from each respective alkaline-activated pumice powder using the conventional linearized Langmuir model (Figure 2) show multiple-sites adsorption (two-sites) with different slopes and intercepts representing the maximum adsorption capacity and related binding strength, respectively. The two-sites Langmuir adsorption isotherm was linearized and rewritten from Equation 1 into Equation 3.

\[
\frac{x}{m} = \frac{b_1 k_1 C}{1 + k_1 C} + \frac{b_2 k_2 C}{1 + k_2 C}
\]  

[3]

where \(b_1\) and \(k_1\) represent respectively the maximum adsorption capacity and binding strength of the first adsorption site, while \(b_2\) and \(k_2\) are of the second site. The value of \(b\) and \(k\) calculated respectively as \(b_1 + b_2\) and \(k_1 + k_2\) (Essington, 2004; Sposito, 2008), are the maximum adsorption capacity and binding strength of the tested adsorbents for Pb.

In summary, Figure 2 shows that for both Lombok and Kediri adsorbents, the curve slopes of the first adsorption site \((y_1)\) are higher than the second one \((y_2)\); while the minimum slopes of both sites were obtained from 0.5 M NaOH activation. The opposite results were obtained for the intercepts. The maximum adsorption capacity and binding strength obtained from the two-sites conventional linearized Langmuir model are shown in Table 1.

Lead maximum adsorption capacity based on the rearranged Langmuir model

Rearranged linearized Langmuir adsorption model as explained by Essington (2004) and Sposito (2008) that uses \(x/mC\) as the y-axis and \(x/m\) as the x-axis can be derived from Equation 4 and Equation 5.

\[
y_1 = \left(\frac{c_1}{c_0}\right)x + \alpha_0 \quad \text{and} \quad y_2 = \left(\frac{c_2}{c_0}\right)x + \left(\frac{\beta_2}{\beta_1}\right)\]

[4]

where \(\alpha_0 = b_1 k_1 + b_2 k_2\); \(\beta_0 = \frac{b_1 + b_2}{k_1 + k_2}\). The adsorption isotherm curves applying the rearranged linearized Langmuir model for the tested adsorbents are given in Figure 3. The lead adsorption parameters derived from fitting the two-sites Langmuir adsorption isotherm using the rearranged Langmuir model are shown in Table 2.

Even though there were differences in \(b\) values acquired from using the conventional and rearranged Langmuir model, the trends remain the same in which the highest \(b\) values of both adsorbents were obtained from 0.5 M NaOH activation. However, the conventional Langmuir model resulted in higher \(r\) values (coefficient of correlation) that indicate a closer relationship between variables representing the lead maximum adsorption capacity than those of the rearranged.
Langmuir model. Therefore, the usage of the conventional Langmuir model was more preferred than the rearranged Langmuir model. By using the preferred conventional Langmuir model, the $b$ value of Lombok adsorbent obtained from $0.5\ M\ \text{NaOH}$ activation was higher than that of Kediri adsorbent. This finding disclosed that Lombok pumice is more promising than Kediri pumice to be utilized as a raw material of lead adsorbent in the solution system.

**Lead removal efficiency in the solution system**

The lead removal efficiency of the tested Lombok and Kediri adsorbents is shown in Figure 4. Overall, the removal efficiency of both adsorbents was more than 80% at Pb initial solution concentration of less than 100 mg.L$^{-1}$ and around 50-80% at 100-260 mg.L$^{-1}$, in which that of Lombok adsorbent was higher than Kediri adsorbent.

![Figure 1](image1.png)  
**Figure 1.** Lead adsorption isotherm curves of Lombok (L, left) and Kediri (K, right) adsorbents prepared from each respective alkaline-activated pumice powder determined using the conventional linearized Langmuir model (0.5, 1, and 2 denote $M\ \text{NaOH}$ concentration).

![Figure 2](image2.png)  
**Figure 2.** Lead adsorption isotherm plots of Lombok (L, top) and Kediri (K, bottom) adsorbents prepared from each respective alkaline-activated pumice powder obtain from the two-sites conventional linearized Langmuir model (0.5, 1, and 2 denote $M\ \text{NaOH}$ concentration).
Figure 3. Lead adsorption isotherm plots of Lombok (L, top) and Kediri (K, bottom) adsorbents prepared from each respective alkaline-activated pumice powder obtained from the two-sites linearized rearranged Langmuir model (0.5, 1, and 2 denote M NaOH concentration).

Figure 4. Lead removal efficiency Lombok (L, left) and Kediri (K, right) adsorbents prepared from each respective 0.5 M NaOH-activated pumice powder at lead solution initial concentrations of 0 to 260 mg.L⁻¹.

DISCUSSION

Pumice is composed of XRD-amorphous silicate minerals with a porous structure (Ismail, El-Shafey, Amr, & El-Maghraby, 2014; Sepehr, Amrane, Karimaian, Zarrabi, & Ghaffari, 2014). FTIR spectra of natural pumice commonly indicates the stretching and bending of Si–O–Si from (SiO₄)²⁻ groups, stretching vibration of –OH groups and H₂O molecules in the lattice, and vibration of H–O–H bond of lattice water molecules (Sepehr et al., 2014, 2013). Its reactive surface ends with
–OH groups and oxygen bridges which perform as adsorption spots (Çifçi & Meriç, 2016).

In general, the values of $b_1$ obtained from applying the conventional, as well as the rearranged Langmuir, the model was lower than $b_2$ while the values of $k_1$ were higher than $k_2$ (Table 1 and Table 2). The lower $b$ and higher $k$ value of the first site as compared to the second site could be explained using the Stern model and triple-layer model (Zhang et al., 2019). Metal adsorption may have occurred on the 0-plane, β-plane or d-plane of the triple-layer model (Criscenti & Sverjensky, 1999). Thus, it could be proposed that the higher $b$ value and the lower $k$ value of the second site than the first one were due to the further distance of the adsorbate to the adsorbent surface. The possible metal surface complexation in the framework of the triple-layer model is that metal cations may bind to deprotonated or neutral surface sites as bare or hydrated metal ions, metal hydroxide complexes, and metal electrolyte anion complexes. In this study, metal-electrolyte anion complexes (between Pb$^{2+}$ and Cl$^-$ from CaCl$_2$) might be formed but not until precipitation occurred. However, according to Speight (2005), the value of reaction quotient, $Q$, of PbCl$_2$ (ranged from $2.3 \times 10^{-13}$ to $3.1 \times 10^{-10}$) is much lower than its corresponding Ksp value ($1.7 \times 10^{-5}$), indicating that precipitation of PbCl$_2$ can not occur. Besides, the equilibrium pH values of the solution systems with initial Pb concentration from 5 to 260 mg.L$^{-1}$ in the present study were varied from 6.05–5.34 and 5.88–5.26 for the usage of adsorbents prepared from Lombok and Kediri pumice powder activated with 0.5 M NaOH, respectively. According to Bradl (2004), Pb(OH)$^+$ is predominant in systems with pH between 6 and 10, while at pH above 9, the formation of Pb(OH)$_2$ is important. It can be stated therefore that precipitation of Pb either as PbCl$_2$, Pb(OH)$^+$ or Pb(OH)$_2$ were not occurring in the present study.

Comparison of the maximum adsorption capacity ($b$ value) of the Lombok and Kediri adsorbent tested in the present study with those of several types of adsorbent reported in the literature, including pumice, is given in Table 3. It shows that both the Lombok and Kediri adsorbents tested in the present study performed higher lead maximum adsorption capacity as compared to the other pumice-based adsorbent, except the pure nano-ball allophane from Japan.

<table>
<thead>
<tr>
<th>Adsorbents prepared from</th>
<th>Activated with</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$B$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lombok pumice powder</td>
<td>0 M NaOH</td>
<td>42.37</td>
<td>144.93</td>
<td>187.30</td>
<td>2.07</td>
<td>0.04</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>0.5 M NaOH</td>
<td>44.05</td>
<td>192.31</td>
<td>236.36</td>
<td>1.82</td>
<td>0.01</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>42.92</td>
<td>156.25</td>
<td>199.17</td>
<td>1.86</td>
<td>0.02</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>2 M NaOH</td>
<td>42.19</td>
<td>149.25</td>
<td>191.44</td>
<td>2.16</td>
<td>0.02</td>
<td>2.18</td>
</tr>
<tr>
<td>Kediri pumice powder</td>
<td>0 M NaOH</td>
<td>40.32</td>
<td>125.00</td>
<td>165.32</td>
<td>2.20</td>
<td>0.05</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>0.5 M NaOH</td>
<td>42.92</td>
<td>175.44</td>
<td>218.36</td>
<td>1.36</td>
<td>0.02</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>42.37</td>
<td>153.85</td>
<td>196.22</td>
<td>2.05</td>
<td>0.02</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td>2 M NaOH</td>
<td>42.02</td>
<td>149.25</td>
<td>191.27</td>
<td>2.33</td>
<td>0.03</td>
<td>2.36</td>
</tr>
</tbody>
</table>

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Table 1. Lead maximum adsorption capacity ($b$ value) and binding strength ($k$ value) of adsorbents prepared from alkaline-activated Lombok and Kediri pumice powder obtained from the two-sites conventional linearized Langmuir model.
The higher maximum Pb adsorption capacity of the Lombok adsorbent than that of Kediri adsorbent can be attributed to their petrology and geochemistry. Based on the volcanic rock petrology and geochemistry data, from the Western Sunda arc to the Eastern Lesser Sunda island, there was a decrease in SiO₂ content (%w), followed by an increase in K₂O, Na₂O, and MgO content (%w) (Dempsey, 2013; Foden, 1979). As reported by Whitford, Nicholls, & Taylor (1979), the K₂O content increase is abundant across the Sunda arc, which indicates the existence of spatial variations in the observed geochemistry, and the transition from calc-alkaline to alkaline lavas (Edwards et al., 1994). The same results were reported by Wheller, Varne, Foden, & Abbott (1987) that from West to East of the West Java, Bali, and Flores arc sectors, each comprises volcanoes which become progressively more K-rich Eastwards. As reported by Aristantha, Hendrawan, & Asmaranto (2017), the chemical composition in percentage of Kediri pumice, determined using AAS, was 81.27 SiO₂, 13.69 Al₂O₃, 3.25 Fe₂O₃, 0.26 FeO₂, 0.59 Na₂O, 0.135 K₂O, and 0.39 MgO, whereas that of Lombok pumice, determined using XRF, was 58.3 SiO₂, 12.4

Table 2. Lead maximum adsorption capacity (b value) and binding strength (k value) of the adsorbents prepared from alkaline-activated Lombok and Kediri pumice powder obtained from the two-sites rearranged linearized Langmuir model

<table>
<thead>
<tr>
<th>Adsorbents prepared from</th>
<th>Activated with</th>
<th>b₁</th>
<th>b₂</th>
<th>b</th>
<th>k₁</th>
<th>k₂</th>
<th>k</th>
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<tr>
<td></td>
<td>(mg.g⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lombok pumice powder</td>
<td>0 M NaOH</td>
<td>30.28</td>
<td>128.64</td>
<td>158.92</td>
<td>3.29</td>
<td>0.02</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>0.5 M NaOH</td>
<td>36.78</td>
<td>149.49</td>
<td>186.27</td>
<td>2.19</td>
<td>0.01</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>25.58</td>
<td>130.94</td>
<td>156.52</td>
<td>4.60</td>
<td>0.02</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td>2 M NaOH</td>
<td>26.26</td>
<td>119.22</td>
<td>145.48</td>
<td>5.15</td>
<td>0.02</td>
<td>5.17</td>
</tr>
<tr>
<td>Kediri pumice powder</td>
<td>0 M NaOH</td>
<td>25.75</td>
<td>100.99</td>
<td>126.74</td>
<td>3.88</td>
<td>0.04</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>0.5 M NaOH</td>
<td>36.55</td>
<td>174.23</td>
<td>210.78</td>
<td>1.57</td>
<td>0.01</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>1 M NaOH</td>
<td>36.60</td>
<td>110.67</td>
<td>147.28</td>
<td>2.32</td>
<td>0.01</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>2 M NaOH</td>
<td>41.34</td>
<td>101.56</td>
<td>142.90</td>
<td>2.56</td>
<td>0.02</td>
<td>2.58</td>
</tr>
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</table>

Table 3. Comparison of Pb²⁺ maximum adsorption capacity of several types of adsorbents obtained from applying the conventional linearized Langmuir model

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>Maximum adsorption capacity (mg.g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allophane, Kumamoto prefecture, Japan</td>
<td>370.40</td>
<td>Elsheikh et al. (2018)</td>
</tr>
<tr>
<td>Alkaline-activated pumice, Kediri, Indonesia</td>
<td>236.36</td>
<td>Present study</td>
</tr>
<tr>
<td>Alkaline-activated pumice, Lombok, Indonesia</td>
<td>218.36</td>
<td>Present study</td>
</tr>
<tr>
<td>Bentonite, Anarak, Iran</td>
<td>71.00</td>
<td>Hamidpour et al. (2014)</td>
</tr>
<tr>
<td>Zeolite, Firouzkoh, Iran</td>
<td>75.00</td>
<td>Hamidpour et al. (2014)</td>
</tr>
<tr>
<td>KCC-1 (fibrous silica nanosphere)</td>
<td>41.61</td>
<td>Hasan and Setiabudi (2018)</td>
</tr>
<tr>
<td>Alkaline-modified pumice</td>
<td>28.09</td>
<td>Jonasi et al. (2017)</td>
</tr>
<tr>
<td>Natural Gisenyi volcanic rock, Rwanda</td>
<td>9.52</td>
<td>Sekomo et al. (2012)</td>
</tr>
<tr>
<td>Natural pumice, Turkey</td>
<td>7.46</td>
<td>Şahan and Öztürk (2014)</td>
</tr>
<tr>
<td>Silica-based adsorbent</td>
<td>5.34</td>
<td>Liu and Wang (2013)</td>
</tr>
<tr>
<td>Natural pumice, Kurdistan, Iran</td>
<td>5.31</td>
<td>Moradi et al. (2015)</td>
</tr>
</tbody>
</table>
The first step is desilication and dealumination which resulted in enhancement of cation exchange sites that explains why adsorbent prepared from Lombok pumice powder has a higher lead adsorption capacity than that of Kediri pumice.

Decreasing lead adsorption capacity with increasing NaOH concentration activation can be explained by the dissolution mechanism of the pumice constituent minerals. As a volcanic material, pumice is commonly composed of allophane and imogolite. These minerals are arranged by short-ranged and poorly ordered aluminum silicates. The reaction mechanism for the dissolution of allophane with alkaline solution occurred in two steps. The first step is deprotonation of alkali ion adsorbed on the silanol group, followed by a nucleophilic attack of Si by hydroxyl ion (Abidin, Matsue, & Henmi, 2004). Si-OH groups are dissociated to form cation exchange retention site, Si–O\(^{-}\), then cation Na\(^{+}\) is adsorbed. The next step is an attack by OH\(^{-}\) toward the pore Si atom whose positive charge has been increased by Na\(^{+}\) exchange (Abidin, Matsue, & Henmi, 2005). Furthermore, Wang et al. (2018) stated that at pH <11.0, preferential dissolution of the polymerized silicates that are mainly occurred, but the dissolved Si and Al are small. At pH >11.0, desilication and dealumination are increasing, resulting in the dissolution of the imogolite local structure (ImoLS) along the edges of the defect pores. In the case of pH = 12.5, more of the ImoLS is dissolved, most of the defect pores are enlarged, some of the secondary pores are disrupted, and some hollow spherules may have collapsed. In this study, increasing NaOH concentrations exceeding 0.5 M during the activation process may develop deprotonation of the Si or Al terminal sites that control the dissolution of the aluminosilicate minerals.

The higher k value of the first site as compared to the second site (Table 1 and Table 2) represents that at similar adsorption rate, the desorption rate from the second site is higher and shows that the binding energy of the first site is higher than second site (Sposito, 2008). The high affinity between adsorbent and adsorbate occurs at the beginning of adsorption process, i.e. when the adsorbent surface covered by the adsorbate is still low and the affinity will decrease with increasing surface closure of the adsorbent by the adsorbate (Essington, 2004; Fonseca, Figueiredo, Rodrigues, Queiroz, & Tavares, 2011; Giles, MacEwan, Nakhwa, & Smith, 1960). The k value, from a practical aspect, can be used as a guide in the regeneration of adsorbent or adsorbate desorption. Desorption study using 0.1 M HNO\(_{3}\) of Gisenyi volcanic rock \((k = 0.014 \text{ L.mg}^{-1})\) yielded desorption percentage of approximately 85% (Sekomo, Rousseau, & Lens, 2012), while that using 0.05-0.2 M HCl on 0.1 M NaOH-modified pumice \((k = 0.052 \text{ L.mg}^{-1})\) was 80-92% (Jonasi et al., 2017; Sekomo, Rousseau, & Lens, 2012). Silva-yumi et al. (2018) disclosed that the higher value of k resulting in the lower desorption percentage.

Lead removal efficiency of the adsorbents tested in the present study were in accordance with that reported by Şahan & Öztürk (2014) that yielded a value of 88.49% at optimum conditions (adsorbent mass 10 g.L\(^{-1}\), initial Pb concentration 84.30 mg.L\(^{-1}\), pH 5.75, and temperature 41.1°C), but higher than those reported by Jonasi et al. (2017); Moradi, Kalantary, Khoosravi, & Sharafi (2015); and Sekomo et al. (2012).
CONCLUSION

The lead maximum adsorption capacity of adsorbents prepared from Lombok and Kediri pumice powder at the most favorable 0.5 M NaOH activation based on the conventional Langmuir model were 236.4 and 218.4 mg.g\(^{-1}\), while those based on the rearranged Langmuir model were 186.3 and 210.8 mg.g\(^{-1}\), respectively. Both adsorbents yielded lead removal efficiency of >80% at Pb initial concentration of <100 mg.L\(^{-1}\) and around 50-80% at 100-260 mg.L\(^{-1}\). It is therefore considered that both pumices are potential to be utilized as raw materials for preparing new natural cationic adsorbent in a solution system with reliable performance.

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