Characterization of Na-P1 zeolite synthesized from pumice as low-cost materials and its ability for methylene blue adsorption

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Abstract. Recently, many researchers have been applied zeolitic materials for dye wastewater treatment by adsorption method because of more practical and economical without requiring a lot of solvents. However, the presence of natural zeolite is limited and only available in a specific area. In this research, pumice stones containing the main components of silicate and aluminate were used as an alternative material to synthesize zeolite. The ability of pumice and zeolite was also tested for adsorbing one of cationic dyes, namely methylene blue (MB). Zeolites were synthesized through the hydrothermal method in high pH conditions and characterized by Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD). The characterization results revealed that the addition of an alkaline solution changed the molecular structure of pumice into Na-P1 zeolite and caused differences in dye adsorption capacity. The adsorption efficiency of pumice was only achieved 65.83% with the MB uptake as much as 5.89 mg/g at the MB concentration of 50 mg/L for 24 hours, while the Na-P1 zeolite was able to adsorb MB molecules almost 100% with the uptake capacity up to 9.12 mg/g.

Keywords: adsorbent, dye removal, environmental science, hydrothermal, wastewater.

1. Introduction

Many industries are commonly used a high quantity of synthetic dyes for coloring their products such as textiles, cosmetics, paper, plastic, and food [1]. Generally, synthetic dyes are more stable compared to natural dyes and making it difficult to degrade by a microorganism. In textile industries, about 10-15 % of dyes will be released as effluents during the coloring process because of not strongly bonded to the textile fiber and finally wasted into the environment [2]. Approximately 750.000 tonnes of dye effluents are discharged annually worldwide [3]. Dye effluent is classified as a toxic compound, carcinogenic, and mutagenic for aquatic organism health. Because synthetic dyes are not easily degraded in water, it can be accumulated to the human body through the food chain [4].
Adsorption technique is often used by experts to manage dye wastewater because this method only uses an adsorbent material without requiring a large number of solvents and energy sources so that it is to be more practical and economical. Lately, many researchers use low-cost materials based on nature, such as rice husk [5], kaolin [6], fly ash [7] and volcanic ash soil [8] to synthesis zeolite due to the high price of SiO₂ and Al₂O₃ compounds as starting materials. According to the previous report, aluminosilicate zeolite can be easily synthesized through the hydrothermal route by applying materials contained SiO₂ and Al₂O₃ in alkaline solution at 80–200 °C [9]. Zeolite has been known as multifunctional materials and mostly applied in many factories. More than 300.000 tons of zeolites are used annually for adsorbing dye effluent [10]. Unfortunately, the availability of natural zeolites is limited and only in specific regions.

One alternative material that can be used to prepare zeolite is pumice. Pumices are categorized as low-cost materials that widely available in Indonesia, such as Bali due to its located in the pacific ring of fire area. The objectives of this research are to synthesize zeolitic material by using pumice stones and use it as adsorbents for the treatment of dyes. Because the main chemical compositions in pumice stones are SiO₂ and Al₂O₃ [11], it is potentially utilized as starting materials to prepare zeolite. However, the type of zeolite produced by using pumice samples from Bali is still unknown and needs to be further characterized. The adsorption ability of zeolite synthesized from pumice samples will also be tested for adsorbing methylene blue dye in solution as a model of dye effluent.

2. Experimental

2.1. Materials

Pumice stones as starting materials were taken from Tempat Pengolahan Akhir (TPA) of Suwung area, Denpasar, Bali, Indonesia. Represented samples were dried and crushed without further purification. All chemicals used in this experiment including methylene blue dye (C₁₆H₁₈ClN₃S) and sodium hydroxide (NaOH) were ordered from Nacalai Tesque Chemical, Kyoto, Japan.

2.2. Synthesis of Zeolite Materials

The synthesis of zeolites was carried out by following the procedure from previously reported with some modifications [12]. In general, pumice samples (10 g) were mixed with an 80 mL of NaOH solution (2.5 mol L⁻¹) and kept on the polypropylene bottle at 100 °C in a drying oven (Mov-212, SANYO) for 24 hours. The product obtained was filtered, rinsed with distilled water for making the pH solution to be 8–9, and dried at 100 °C for 12 hours. Zeolite powder obtained was crushed and separated using standard sieve of 100 mesh.

2.3. Materials Characterization

The Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) were used to characterize both samples (pumice stone and synthesized product). Specifically, the functional groups in represented samples were analyzed by using an FT-IR spectrophotometer (Perkin Elmer Spectrum One, Massachusetts, USA) ranging from 500–4,000 cm⁻¹, while the mineral phases of both samples were identified by an X-ray diffractometer (Bruker D8, Texas, USA) with Cu Kα radiation at 40 kV, 30 mA and 20 ranging from 5–50° at a scanning speed of 2°/min.
2.4. Methylene Blue Adsorption
The adsorption capability of both samples was tested for adsorbing MB solutions (25 and 50 mg/L) at room temperature. About 10 mL of MB solutions were put into test tubes containing 50 mg of solid samples while shaking for a few minutes. The adsorption process was investigated for 24 hours. The treated solutions were centrifuged for 10 minutes and the final MB concentrations were determined by a spectronic 20D+ spectrophotometer. The adsorption efficiency (%A) and the amount of MB uptake (qe in mg/g) were calculated by following equation 1 and 2, respectively.

\[ \%A = \frac{(C_0 - C_e) \times 100}{C_0} \]  \hspace{1cm} (1)

\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]  \hspace{1cm} (2)

Where \( C_0 \) and \( C_e \) are initial dye concentration (mg/L) and equilibrium dye concentration (mg/L), respectively, \( m \) is the mass of samples (g) and \( V \) is a total volume of MB solution (L).

3. Results and Discussion

3.1. Materials Characterization
The XRD pattern of both samples is represented in figure 1. These results verified that there are significant changes in mineral phases of pumice samples before and after alkaline addition. According to the pumice sample XRD pattern, it contains a lot of amorphous materials and no characteristic peaks appear. However, the pumice sample which treated alkaline solution following by hydrothermal process has been successfully formed characteristic peaks of Na-P1 zeolite at 12.46°, 17.66°, 21.67°, 28.10°, 33.38°, 38.01°, 42.2° and 46.08°. It is compared and confirmed by Na-P1 zeolite phases from International Zeolite Association (IZA) with 2θ degree = 12.46°, 17.66°, 21.67°, 25.08°, 28.10°, 30.84°, 33.38°, 35.76°, 38.01°, 40.15°, 42.20°, 44.18°, 46.08° and 49.72°.

The FT-IR spectra of both materials are displayed in figure 2, which recorded from 500–4,000 cm\(^{-1}\). For the pumice sample (a), the peaks at ~720, 1000, 1650 and 3475 can be described to the bending vibration of Si-O-Si bond, the symmetric stretching vibration of Si-O-Si in (SiO\(_4\))^2- groups as a characteristic peak, the bending vibration of H-O-H bond and the asymmetric stretching vibration of O-H bond, respectively. Although both of material have similar FT-IR spectra, there are several different peaks which appear especially in fingerprint area (500–1500 cm\(^{-1}\)) of the synthesized Na-P1 zeolite. A double ring vibration at 595 cm\(^{-1}\) showed that the zeolitic phase was produced, while the vibration peaks at 680 and 745 cm\(^{-1}\) indicated to the symmetric stretch of T-O-T bond (T = Si, Al) in Na-P1 zeolite framework [13].
Figure 1. XRD pattern of (a) pumices, (b) the synthesized Na-P1 and (c) pure Na-P1.

Figure 2. The FT-IR spectra of (a) pumices and (b) Na-P1 zeolite.
3.2. Adsorption of MB Dye

The adsorption process is carried out in MB concentrations of 25 mg/L and 50 mg/L at room temperature for 24 hours. The adsorption results showed that pumice samples can be directly used to adsorb MB molecules even in small capacities (figure 3a and 3b). This condition can be explained because of the abundance of SiO$_2$ content in pumices making its surface tend to be negatively charged and the methylene blue, which is a cationic dye, can be adsorbed even in small capacities. According to Asgari et al. [14], pumice has negative zero potential under both acid and alkaline conditions in the range pH of 2–12 where the isoelectric point cannot be determined in any conditions. It confirms that pumice surfaces contain permanent negative charges. The isoelectric point is considered as a point where there will be a change in the surface charge [15].

![Figure 3](image)

**Figure 3.** Adsorption of MB molecules for 24 hours: (a) initial MB concentration (50 mg/L), (b) by using pumices and (c) Na-P1.

Adsorption efficiency of MB molecules using pumice is much lower than synthesized Na-P1 zeolite if we compare it by the intensity of MB color (Fig. 3b and 3c). This condition can be explained because pumice samples were collected without further purification and still contained many impurities, thus affecting its ability to adsorb MB molecules. However, the alkaline addition which followed by heating and washing process to produce Na-P1 zeolite has been successfully removed the impurity content and also increased the active site of material. Hence, pumice samples can uptake a small portion of MB molecules compared to the synthesized Na-P1 zeolite. At MB concentrations of 50 mg/L, the adsorption efficiency of pumice samples was only 65.84% with the uptake capacity about 5.89 mg/g, whereas the synthesized Na-P1 zeolite was reached 99.98% with the MB uptake as much as 9.12 mg g$^{-1}$ (figure 4). The modified pumice stone with a hydrochloric acid solution has also been conducted by Derakhshan et al. [16] to adsorb MB dye from aqueous solutions in the concentration of 50 mg L$^{-1}$. The adsorption result showed that the modified pumice can adsorb MB molecule about 92.3%. Therefore, the transformation of pumice structures into zeolite framework in this work is considered more effective for adsorbing cationic dyes than modified pumice using acid solutions.
3.3. Adsorption Mechanism

Zeolites are aluminosilicate minerals whose crystal structure consists of tetrahedral units, in which either $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ are interconnected through oxygen atoms. The isomorphic substitution ability of $\text{Si}^{4+}$ which can be replaced by $\text{Al}^{3+}$ produces a negative charge that makes zeolites easily bond with other cations. The negative charge on zeolites is permanent and does not depend on the pH condition. On the other hand, methylene blue dyes are classified as a cationic dye because they would be ionized in water by carrying a positive charge. The proposed mechanism of methylene blue adsorption onto Na-P1 zeolite is represented in figure 5.

![Figure 5. Methylene blue dye adsorption mechanism onto Na-P1 zeolite](image)

Because zeolite has negative charges on its surface, it easily absorbs cationic dyes in water, such as MB dye. The more negative charge available on zeolites, the higher adsorption capacity to uptake cationic dyes. In this work, the synthesized Na-P1 zeolite was able to adsorb MB molecules almost 100%, which confirms that zeolite contains many negative charges on its surface.
4. Conclusion
Na-P1 zeolites have been successfully synthesized by using pumice samples through the hydrothermal method in high alkaline condition. Based on the adsorption data, the synthesized Na-P1 zeolite has a higher ability to adsorb MB molecules than starting materials. The use of pumice samples as adsorbent was only able adsorbing MB molecules in a low capacity about 5.89 mg/g with the adsorption efficiency of 65.83% at MB concentrations of 50 mg/L for 24 hours, while the amount of MB uptakes by Na-P1 zeolite reached 9.12 mg/g where the adsorption efficiency was almost 100%.

5. References
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