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Comparative Study of Natural Zeolite, Activated Carbon and Green Sand as a Catalyst Support for Ozone Decomposition

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Abstract. This research is based on ozone emissions from drinking water and bottled water and disinfection processing in the dairy and food industries, which endangers living things and destroys the environment. Ozone decomposition uses manganese oxide (MnOx) as an active site with 0–2% of nominal loading. Three kinds of catalyst support (Lampung Natural Zeolite, Granular Activated Carbon and Green Sand) with 18–100 diameter mesh were compared. The catalyst was prepared by incipient wetness impregnation and calcination at 300°C and its performance in the conversion of ozone decomposition was tested in a continuous fixed bed reactor. It was found that granular activated carbon as the catalyst support, with 60–100 diameter mesh and 1% loading nominal with decomposition conversion of 100% for 24 hours was the most effective and efficient method. Meanwhile, LNZ and GS which has the same variables, only have 76.98% and 86.18% in conversion for the 1-hour decomposition process. The catalysts that were GAC, LNZ and GS, furthermore analyzed by BET and SEM EDX methods. The results were 558.754 m²/g, 40.931 m²/g and 5.557 m²/g in surface area and 0.47%, 0.11% and 0.95% in actual loading, respectively.

INTRODUCTION

Ozone is purposely produced for the sterilization process of the mineral water industry in Indonesia, and worldwide it is used as a disinfectant in the dairy and food industries. 2–3 ppm of dissolved ozone is used in raw food washing (Bhataraj, 2001). Technically, the maximum dissolved ozone is only 0.4 ppm in mineral water. Bhataraj states that the concentration of water-soluble ozone is only 4.29 ppm from 6.044 ppm added at a temperature of 20°C (Bhataraj, 2001), so the ozone residue that is not dissolved can endanger the working environment. Ozone exposure will damage the respiratory system and irritation to the eyes and skin in human and increase aquatic toxicity in the surroundings. The maximum ozone exposure for humans is 0.10 ppm for 8 hours, or 0.30 ppm for 15 minutes (Ozone Solutions, 2005).

Residual ozone can be decomposed catalytically. MnOx as a catalyst is highly efficient and has a high potential oxidation-reduction number that can be used even at ambient temperatures and high humidity. However, the surface

area cannot be controlled and the catalytic activity is not based on the exposed surface area (Dhandapani, et al., 1996). Lampung Natural Zeolite (LNZ), Granular Activated Carbon (GAC) and Green Sand (GS) used as catalyst supports have high adsorption capacities and relatively low prices. LNZ with a Si/Al ratio below 8 (Bismo, 1997) has better catalytic activity than some known zeolite compounds with Si/Al ratios above 8 (Kusuda, et al., 2013). GS has an Mn content that contributes to ozone decomposition. Catalyst qualities are based on the surface area, which is characterized by the BET method, and catalyst surface and catalyst composition, which are analyzed by the SEM EDX method. Catalyst performance is shown by ozone decomposition conversion in a fixed bed reactor, influenced by the hydrodynamic phenomenon.

The quality and performance of the catalysts for these three types of catalyst support are compared in this study. Quality refers to catalyst diameter, pore diameter, pore volume, surface area, actual loading concentration and catalyst composition, while the performance of the catalyst is based on the conversion of the ozone decomposition.

MATERIALS AND METHOD

Materials

Lampung Natural Zeolite, Granular Activated Carbon and Green Sand catalyst support samples with diameters of 18–35 mesh, 35–60 mesh and 60–100 mesh, and %-nominal loadings of MnOx of 0%-w, 1%-w and 2%-w from KMnO_4 (potassium permanganate) solution were used. The supports were prepared by using deionized water, NaOH 0.05 M (sodium hydroxide) and HCl 0.05 M (hydrochloric acid). Ozone concentration was determined by the iodometric method, which requires KI 0.1 M (potassium iodide), H_2SO_4 2N (sulfuric acid), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (sodium thiosulphate) and an amylum indicator. Pro analyst grade chemical reagents were used for analysis and technical grade quality for the raw materials and treatment reagents.

Catalyst Preparation Method

The catalyst support was pulverized until the desired size was obtained. It was activated by soaked in deionized water, HCl 0.05 M, and NaOH 0.05 M for 30 minutes respectively, a total of 90 minutes. After being soaked in each solution, it was filtrated and washed in deionized water, then dried in a vacuum oven. Subsequently, manganese as an active site attached to the catalyst support by impregnated with KMnO_4 solution (concentration based on the nominal loading) for 12 hours at ± 200 rpm impeller speed. Next, the catalyst was filtrated and heated at 300°C for 4 hours before being cooled in a desiccator before use.

Catalyst Performance Test Method

The fixed bed reactor was filled by 5 mL catalyst. Air was then fed into the ozone generator and changed into ozone gas feed in the reactor at a flow rate of 3 Lpm for an hour. The ozone decomposed in the fixed bed reactor and oxygen as the residue in the outlet was trapped by the KI solution. Ozone concentration before and after passing through the reactor was determined by the iodometric method (see Fig. 1).

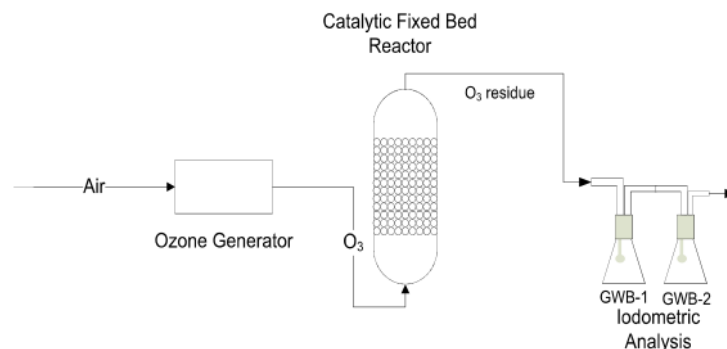


FIGURE 1. Equipment scheme for ozone productivity test

Ozone concentration with and without the catalyst was calculated using equation (1), and the conversion of ozone calculated by equation (2).

$$\text{Ozone Concentration} = \frac{I}{2} \cdot V_{\text{thiosulfate}} \cdot M_{\text{thiosulfate}} \cdot BM_{\text{ozone}} \cdot fp \cdot fw \quad (1)$$

where fp is the diluted factor in titration and fw is the time factor.

$$\text{Ozone Conversion} = \frac{\text{Concentration}_{\text{ozoneinlet}} - \text{Concentration}_{\text{ozoneoutlet}}}{\text{Concentration}_{\text{ozoneinlet}}} \quad (2)$$

RESULTS AND DISCUSSION

Catalyst Quality

BET Test Results

A BET test was conducted to determine pore diameter, pore volume and catalyst surface area. The results in Fig. 2 show that the activation method for LNZ and GS worked only on the surface of the catalyst support by changing pore diameter size, but not the number of pores. This was because of the desilication and dealumination as an effect of the activation process. Cation exchange could decrease the surface area (Bismo, 2000), in which Mn fills in the catalyst support structure. Ates, et al. (2016) reports that the catalyst structure could be deformed and the surface area decreased, although the pore diameter increased if desilication and dealumination occur at the critical state. LNZ has 71.77% clinoptilolite (Bismo, 2000), which has a lower thermal resistance than modernite or analsim (Saksono, et al., 1997) so it could deform during calcination. The catalyst supported by GS indicates the occurrence of sintering when it could not be heated at a temperature of 300°C for 4 hours. Hassan (2004) reported that sintering did not occur when heated at 550°C for 2 hours, while the structure of the catalyst supported by GAC changed with the new pores were formed. The smaller the size of the catalyst, the higher it's quality. For comparison, GAC with a 60–100 mesh diameter has a higher quality than 18–35 mesh size. However, one cycle of regeneration of the catalyst supported by GAC could increase its overall quality. Therefore, the bigger diameter catalyst that was regenerated could have reached the quality of the smaller one.

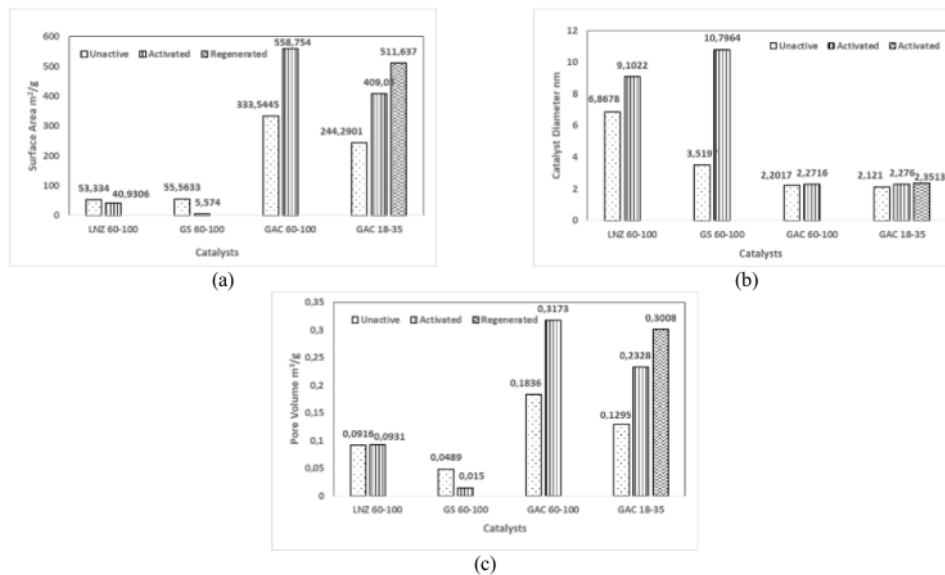


FIGURE 2. BET Test Results for Nominal Loading Concentration 1%; Surface Area m²/g (a), Catalyst Diameter nm (b) and Pore Volume m³/g (c)

SEM EDX Test Results

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The SEM test was conducted to capture the morphology of the catalyst before and after the activation process, while the EDX test determined the composition of the catalyst at a certain point. Figs. 3 and 4 show that the catalyst support (LNZ and GS) is free from impurities, and catalyst holes are clearly seen. As shown in Fig. 5, after activation the surface had many holes; activation and the calcination process destroyed the GAC structure, so new holes were formed.

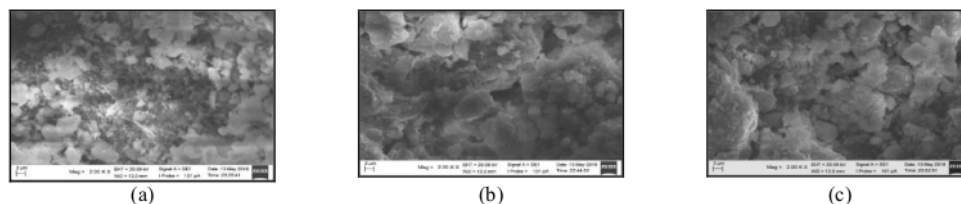


FIGURE 3. SEM Test Results LNZ 60-100 mesh 1% (a) before activation (b) after activation (c) after decomposition test

The EDX test showed the composition of the catalyst at one point (Table 1). Based on the results, the percentage of the elements in the catalyst was changed. The amount of carbon in the LNZ and GAC increased after activation because the calcination process formed coke which is bonds of carbon and oxygen. However, the amount of carbon decreased after the decomposition test because it reacted with the ozone to form CO and CO₂ which were desorbed from the catalyst.

TABLE I. EDX Catalyst Test Results

Element	LNZ			GS			GAC			
	Unactive	Loading 1%	After Test	Unactive	Loading 1%	After Test	Unactive	Loading 1%	After Test	Loading 2%
C	6.72	14.54	2.72	4.97	2.53	2.91	81.34	84.44	69.65	77.25
O	47.17	51.05	52.31	49.07	55.83	51.45	9.42	12.71	22.86	19.77
Na	0.03	0.54	0.42	1.34	2.36	1.30	0.75	0.28	0.90	0.30
Al	6.88	5.79	7.32	7.37	7.47	7.62	0.00	1.04	2.84	0.49
Si	31.18	23.75	30.69	27.30	25.18	27.09	0.13	0.11	0.20	0.00
Mn	0.00	0.11	0.43	1.33	0.95	1.59	0.00	0.47	0.37	1.07

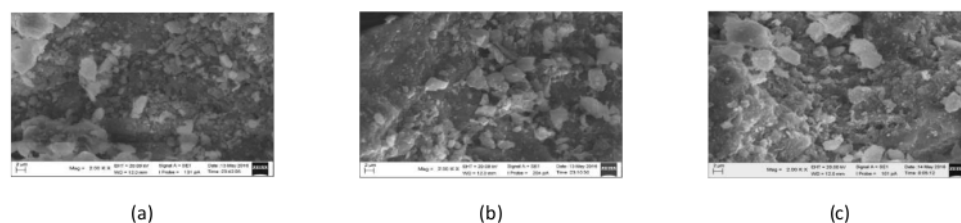


FIGURE 4. SEM Test Results GS 60-100 mesh 1% (a) before activation (b) after activation (c) after decomposition test

The sodium content increased due to the washing process that used NaOH 0.05M. This process caused desilication to occur, although at a low level, then Na metal was deposited in the catalyst. Mn metal actual content becomes half than the nominal loading because KMnO₄ as a precursor was not absorbed well into the catalyst support and cation exchange of Mn²⁺ as balance cation has slightly occurred. The Mn content decreased after activation (GS) because it was soaked in HCl 0.05 M so was dissolved along with the filtrate. However, the Mn content is still higher than the nominal loading content because GS as the supported catalyst already contained manganese metal before activation. Basically, the GAC did not contain aluminium, but the aluminium material plate used in the heating process affected the occurrence of aluminium metal deposition.

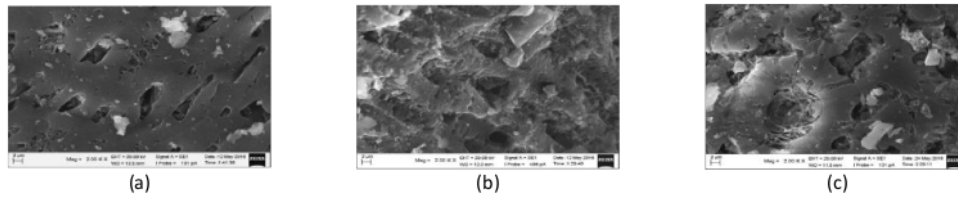


FIGURE 5. SEM Test Results GAC 60-100 mesh 1% (a) before activation (b) after activation (c) after decomposition test

Catalyst Performances

The catalyst with the highest performance was that 60-100 mesh in size. This was because the smaller sized catalyst resulted in a larger surface area. The catalyst support with a nominal loading of 1% has higher performance than nominal loading of 2% because the catalyst already saturated with the active site and catalyst support made the smallest contribution to the ozone decomposition process. Wang (2014) also reports that a nominal loading of 1.1% of MnOx with activated carbon support has the best performance. Although MnOx/GS displays sintering, it has a better performance than MnOx/LNZ because of its higher Mn content, which contributed to the decomposition process. Activation of the LNZ catalyst did not include cation exchange, whereas Valdes (2012) states that using balanced cation exchange with NH_4^+ would increase Lewis acid site, which plays an important role in ozone decomposition.

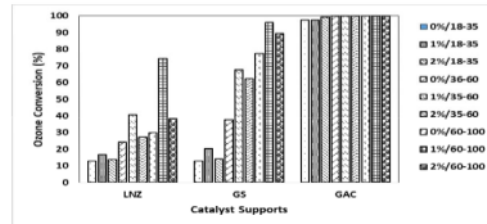


FIGURE 6. Conversion of catalyst decomposition towards the types of catalyst support

The Effect of Regeneration in GAC

The GAC catalyst support showed the best performance in ozone decomposition during one hour test. The MnOx/GAC/1%/60-100 still has 100% conversion of ozone decomposition while MnOx/LNZ/1%/60-100 has 76,98% and MnOx/GS/1%/60-100 has 86,18%. Because of this, the time test of GAC catalyst extended for 24 hours resulting 100% conversion. Catalyst MnOx/GAC with 18-35 mesh diameter of the catalyst support, nominal loading concentration of 1% and process time of 8 hours, regenerated physically by calcination at a temperature of 300°C for 4 hours, produced significantly increased catalyst characteristics. Deactivation of the catalyst because of the CO and CO_2 formed during decomposition with a slow desorption rate of CO and CO_2 (Heisig, et al., 1997) could lower the catalytic activity. According to BET test, GAC catalyst has the largest surface area and pores volume. The porous lichen-like morphology (Wang, 2014) makes a lot of ozone easier going through the inside catalyst which then decomposed.

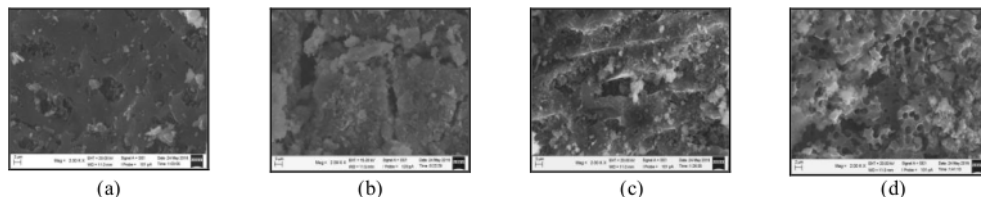


FIGURE 7. Morphology of GAC 18-35 mesh 1% Before Activation (a) After Activation (b) After Decomposition Test (c) and After Regeneration (d)

Figure 7 shows that more holes formed after the regeneration process and that the surface area must be higher than before (see Fig. 2). This means that GAC can be regenerated by just using physical calcination. Table 2 shows that the Mn actual loading is higher than its nominal loading. It because the precursor could not be absorbed evenly by the catalyst support. The element content after regeneration was not very different than after test but the catalyst physically changed.

TABLE 2. EDX Granular Activated Carbon (GAC) Test Results

Element	GAC 18-35 mesh			
	Unactive	Loading 1%	After Test	After Regeneration
C	89.16	19.47	50.79	53.86
O	7.64	45.93	37.69	35.30
Na	0.46	0.74	0.13	0.77
Si	0.09	0.00	0.21	0.36
Mn	0.00	5.43	1.82	0.90

CONCLUSION

Based on the research results presented, it can be concluded that a nominal loading of 1% is the optimum concentration, although the loading absorption ability is not optimal and is uneven. Related to the conversion of ozone decomposition, the catalyst performance of MnOx supported by GAC is the highest, with 100% conversion during 24 hours for catalyst support 35–100 mesh in diameter and with a nominal loading concentration of 0–2%. In comparison, LNZ and GS catalysts did not reach 100% conversion for one-hour decomposition test. The catalyst quality can be seen in the larger surface area, pore volume, pore diameter and the optimum actual loading. The size of the catalyst affected catalyst performance. A smaller sized catalyst results in a higher performance because the surface area is larger. Moreover, the smaller the catalyst size, the higher the pressure drop. Therefore, the contact time of the ozone with the catalyst increases and with a lower amount of ozone contacted, catalyst performance could increase.

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