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Development of Porous Ceramic Diffuser from Red Clay, Diotomite and Rice Hull Ash Mixtures using Slip Casting Method

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Abstract

A red clay-based porous ceramic for water aeration diffuser application was produced from different compositions of Lama-Lama clay, Kapatagan diatomite, and rice hull ash. The formulations were based on the clay to silica ratio of 40/60, 45/55, 50/50, and 55/45. Low-cost additives like cornstarch and cassava starch were also added as pore formers at 15 weight percentage. Cylindrical and rectangular test pieces were made by slip casting that was fired at 1050^oC and 1150^oC. The solid casting of slip was done by heating in a microwave oven at 60^oC and 80^oC, respectively. Various tests were conducted on the fired specimens such as firing shrinkage, water absorption, apparent porosity, bulk density, specific gravity, modulus of rupture, and scanning electron microscopy. The best formulation appropriate for air diffuser was the sample with the composition of 55/45 clay to silica ratio without starch and was fired at 1050^oC.

Keywords: ceramic diffuser, diatomite, red clay, rice hull ash, slip casting

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1. Introduction

One of the problems involving global warming is the release of wastewater from industrial, commercial and residential sources to our environment. These waters should undergo rehabilitation by aeration, and one way is to employ porous ceramic diffusers using red clay-based materials. Consequently, this study was made because of its great impact on our environment when it will be put into use.

In aeration, air or oxygen-enriched air is introduced into wastewater in several unit processes designed for contaminant removal and may be used either to satisfy the biochemical oxygen demand in biological treatment processes or to act as an agent in the oxidation of undesirable contaminants. One of the aeration applications in wastewater treatment is through diffused aeration which is defined as the injection of gas, either air or oxygen, below a liquid surface or the generation of gas bubbles emanating from pores or orifice openings submerged in a basin of water. In the past, various devices commonly were classified as either fine bubble or coarse. Currently, the industry prefers to categorize air diffusion systems by the physical characteristics of the equipment, namely, porous diffusers, nonporous diffusers, and others (Hendricks, 2011; Vesilind, 2003).

However, the most interesting devices of air diffusion are the porous ceramic diffusers. A number of studies were conducted on the development of porous ceramics from alumina and silica rich materials. Glass-ceramic composites were produced based on metallurgical slag and TV waste glass which could be a potential material for diffusers in water aeration procedure because of its high durability in acid and alkali solutions as well as in water (Mangutova *et al.*, 2004). Another research used quartz sand and waste glass to form porous composites with controlled porosity and interconnected pores which can also be used for production of air diffusers for water aeration (Adžiski *et al.*, 2008) Accordingly, porous ceramic for bubbling air into water at 1 bar of pressure was successfully developed from quartz that was added to help with strength and clay to assist in forming (Küçük, 2009).

Ceramic forming technique such as slip casting is one of the versatile processes that can be successfully applied to shape porous ceramics (Colombo *et al.*, 2010). Few reports has been done on the preparation of ceramic diffusers that are red clay-based have been published. The marketed ceramic diffusers are generally made from compounds which have a relatively elevated cost. In this work, the diffusers were manufactured from indigenous raw materials in order to lessen the cost and to assess our natural resources. This study aims to fabricate porous ceramics from available local materials for water aeration diffuser applications in terms of physical and chemical properties based on the best formulation via slip casting method.

The formulation studies were carried out on a three-factor factorial design (Excel, 2012) to investigate the effects of the following factors like temperature, forming method, type of starch used and composition on the properties of the prepared porous ceramic red-clay bodies. Composition percentage of various mixtures was based mainly on the clay to silica (diatomite/RHA) ratio. It was assumed that the porosity is affected by the weight percent of raw materials. Moreover, statistical procedures were utilized to analyze and interpret the data like weighted mean, percentage and ANOVA (Montgomery, 2001; Tiin, 1996).

2. Methodology

The starting materials used in this investigation were Lama-lama red clay from Tubod, Lanao del Norte and diatomite from Kapatagan, Lanao del Norte. Rice hull ash (RHA) from raw rice husk fired at 700-800^{o}C were obtained from the Ceramic Training Center of MSU-IIT, Iligan City, Philippines. The cassava starch and corn starch were bought from stores, FK Mart and Gaisano Mall, Iligan City, respectively. These raw materials were stored in plastic sacks and containers for further use. The chemical oxide compositions of the raw materials are given in Table 1 while the chemical analysis for cornstarch is 26.30% amylose, 0.07% N, 0.05% ash, 0.12% fat, and 8.72% moisture and that of cassava is 0.24% ash, 0.13% fat, 0.49% protein, 0.15% crude fiber and 98.4% amylopectin (Gregorová *et al.*, 2006).

Table 1. The chemical oxide composition of the raw materials: Lama-Lama clay (LC), Kapatagan diotomite (KD), and rice hull ash (RHA)

Chemical Analysis	% Composition		
	LC	KD	RHA
SiO_2	35.64	69.82	95.89
Al_2O_3	22.77	11.46	0.30
Fe_2O_3	12.22	10.61	0.25
MgO	0.31	1.01	0.38
Na_2O	0.06	0.95	0.04
K_2O	0.04	1.40	1.77
TiO_2	1.04	0.76	0.01
BaO	0.08	0.66	-
MnO	0.02	0.05	0.20
P_2O_5/ SO_3	0.02/0.06	0.16/0.06	0.54/0.10
LOI	27.40	2.06	-

2.1 Slip Casting

The raw Lama-Lama clay and Kapatagan diatomite were pulverized separately and then sieved to pass through 70 mesh screen to ensure uniformity. They were batched together with the other additives like RHA and starch as shown in Table 2 in a plastic bag with a batch weight of 300 grams and stored in plastic containers. The batched materials were then combined slowly with water using an electric hand mixer with a solid loading of 52%. The mixtures were then blunged and 0.70-1.0% sodium silicate was added as deflocculant. A good slip was maintained having a specific gravity of 1.32-1.36 for a red clay-based slip with diatomite and then aged for one day. The slip was remixed, and the rheological data of the slurry was determined using a viscometer with spindle #4. Afterwards, the slip was poured into a plaster mold. About six samples per formulation were made, and castings were carried using solid casting method out at 60^{o}C in a resistance temperature detector (RTD), microwave oven for 8-10 minutes. The solid cast samples were demolded after 10 minutes or when the cooling temperature reached 40^{o}C. The damp newspaper was used to cover each sample to prevent abrupt air drying.

Table 2. Mixture compositions for slip cast (SC) samples

Code No.	Lama-Lama Clay (%)	Kapatagan Diatomite (%)	Rice Hull Ash (%)	Corn Starch (%)	Cassava Starch (%)
SC1	40	55	5	15	-
SC2	45	50	5	15	-
SC3	50	45	5	15	-
SC4	55	40	5	15	-
SC5	40	55	5	-	15
SC6	45	50	5	-	15
SC7	50	45	5	-	15
SC8	55	40	5	-	15
SC9	40	55	5	-	-
SC10	45	50	5	-	-
SC11	50	45	5	-	-
SC12	55	40	5	-	-

2.2 Drying and Firing

The test sample formulations were air dried for seven days and oven dried for 4 hours at 110^{o}C to ensure that the specimens were nearly moisture-free. The green test samples were fired at two temperatures namely, 1050 and 1150^{o}C using a Vecstar electric muffle furnace, Chesterfield, United

Kingdom. The samples were fired very slowly with an hour soaking time at 300, 400, 500 and 600^{o}C until the firing temperature was reached.

2.3 Machining

Final machining was done manually to all cylindrical disc fired samples for initial bubble formation trials using an electric grinding machine to attain the optimum fit of the disc inside the improvised diffuser set-up.

2.4 Characterization

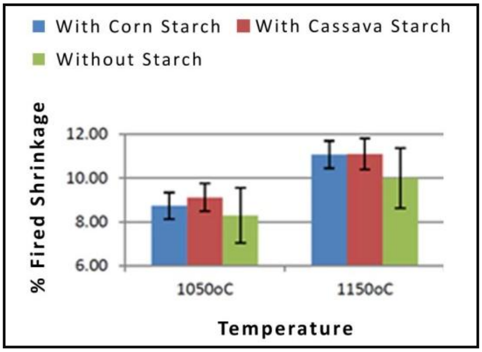
For each formulation, physical properties like dry shrinkage, firing shrinkage, water absorption, apparent porosity, bulk density, specific gravity, and modulus of rupture were measured on the fired specimens. All these tests were based on the methods from American Society for Testing and Materials (ASTM) (ASTM International, 2006; ASTM International, 2009). The morphology and microstructure of present phases after firing were identified using SEM-EDX (Analytical Scanning Electron Microscope with Energy-Dispersive X-ray Spectrometry Analyzing System, JSM-6510LA, JEOL Ltd., Japan). The samples were coated with platinum using Autofine Coater Plasma JFC-1600 before mounting and photomicrographs were taken.

3. Results and Discussion

This study involved the investigation of the effects of variables namely starch used at three levels which are corn starch, cassava starch, and non-starch; composition at four levels that are 40/60, 45/55, 50/50, and 55/45 clay to silica ratio; and temperature at two levels 1050^{o}C and 1150^{o}C, respectively. Three replicates of a factorial design are run in these factors, with all twenty-four runs took in random order. The responses sought after were firing shrinkage, modulus of rupture, water absorption, apparent porosity, bulk density, and specific gravity of the red clay-based porous ceramic material.

3.1 Firing Shrinkage

As shown in Figure 1, contraction is observed which increases with the rise in temperature (Reed, 1995). Samples made by slip casting require a greater amount of water as a binder, and so have higher fired shrinkage. This illustrates that more adsorbed water is eliminated that caused more shrinkage. Increasing clay to silica ratio from 40/60 to 55/45 resulted in the decrease in fired shrinkage of the samples. This is contradictory to the common observation but since diatomite is added at decreasing percentage then maybe it contributed to lower shrinkage. Furthermore, due to a large amount of burning agents, firing shrinkage of the starch-containing samples is always relevant than non-starch containing samples.



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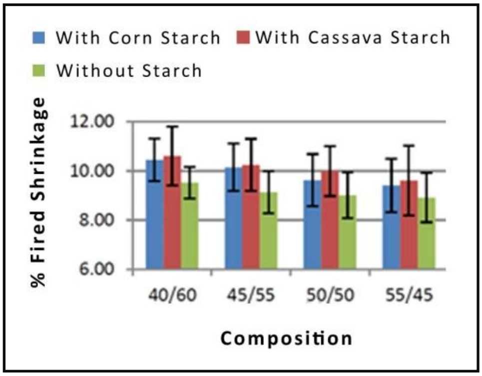
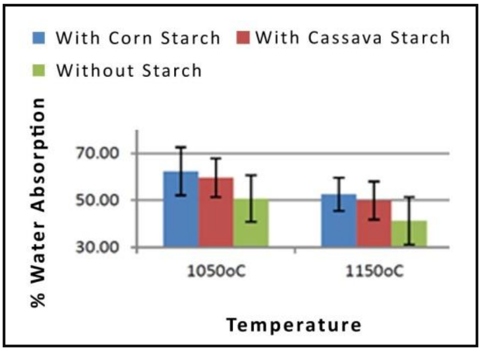


(b)

Figure 1. Effects of (a) temperature and (b) compositionon the fired shrinkage of the starch-containing and non-starch containing samples

3.2 Water Absorption

The results concerning the test of water absorption in samples as a function of the temperature, as presented in Figure 2, shows that increasing the temperature from 1050 to 1150°C yields decreasing water absorption which is due to densification. Above 1050°C, water absorption is associated with liquid phase formation wherein it penetrates the pores, closing them and isolating neighbouring pores. The liquid surface tension and capillarity help to bring pores close together and reduce porosity. These particles undergo a rearrangement that promotes densification and contraction of the internal structure and so explains the decrease of the water absorption in this temperature range (Baccour *et al.*, 2008). High values of water absorption obtained in this study indicate that the bodies produced are highly porous (Karaman *et al.*, 2006). Also, lower clay with higher silica content corresponds to higher percent water absorption values. This is influenced by the addition of diatomite which is naturally porous. Starch containing bodies have higher percent water absorption than non-starch containing samples due to the burnout of starch.



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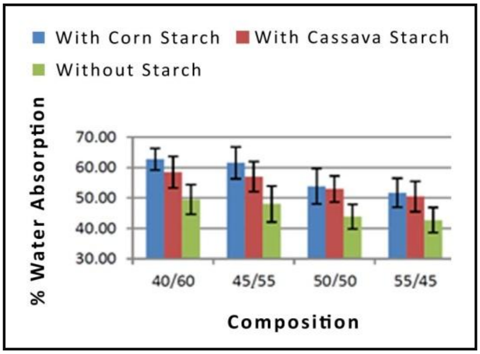

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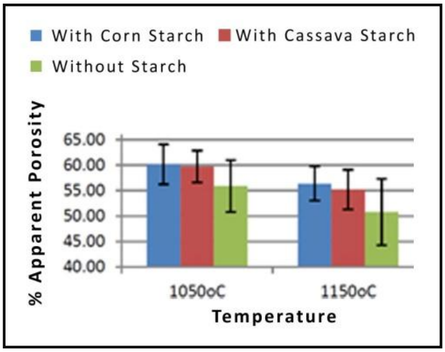
Figure 2. Effects of (a) temperature, and (b) composition on the water absorption of the starch-containing and non-starch containing samples

3.3 Apparent Porosity

Percent apparent porosity (Figure 3) of the bodies is inversely proportional to the firing temperature since increasing temperature from 1050 to 1150°C decreases apparent porosity which is due to densification. Furthermore, at lower clay and higher silica composition of 40/60, formulated bodies have higher percent apparent porosity values. In this study, the natural porous structures of diatomite that act as source of silica have immensely contributed to the porosity. Another observation is that starch containing bodies have higher apparent porosity as compared to formulations without starch, thus, addition of starch corresponds to increase in porosity of ceramic substrates. Samples have higher porosity after heating than the nominal starch content, which is a clear indication of starch swelling accompanied by a corresponding increase in the average pore size (Gregorová, *et al.*, 2006).



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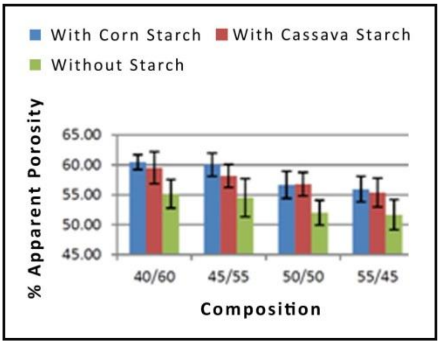
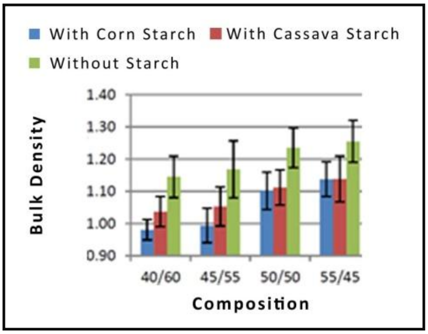


(b)

Figure 3. Effects of (a) temperature , and (b) composition in the apparent porosity of the starch-containing and non- starch containing samples

3.4 Bulk Density

The increase in temperature from 1050 to 1150°C yields high bulk density of formulated bodies as presented in Figure 4 and is correlated with the decrease in porosity as observed. During sintering, bulk transport will create a change in the interparticle spacing as neck growth takes place. The result is shrinkage, increased density, and higher strength for the entire powder compact. Longer times, higher temperatures, and higher initial packing densities all contribute to a higher sintered density (Schneider, 1991). Also, bulk density is highest at compositions 55/45 and lowest at 40/60 clay to silica ratio. Thus, higher clay content resulted to increase in bulk density while higher silica content of diatomite and rice hull ash leads to decrease in bulk density and this is maybe due to its porous structure and lightweight property (Garderen *et al.*, 2011).



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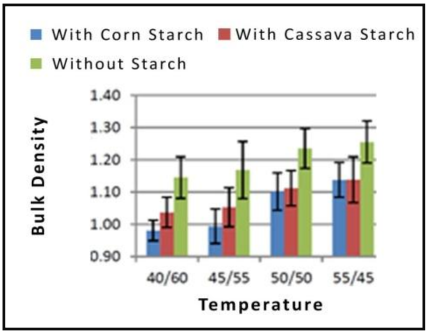

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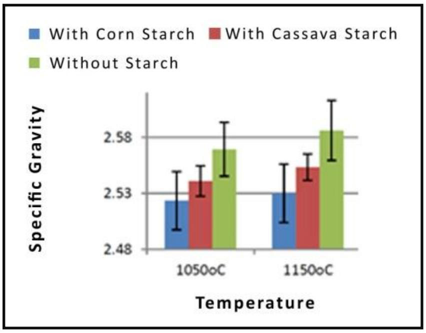
Figure 4. Effects of (a) temperature, and (b) composition in a bulk density of the starch-containing and non-starch containing samples

3.5 Specific Gravity

The specific gravity (Figure 5) values of all formulated bodies are unaffected by temperature, forming method, and composition except for corn starch containing bodies. This might be due to the fired products which have almost the same structure or phases as with the other formulations. Higher clay content and lower silica content also leads to higher specific gravities as illustrated in Figure 5 which are also proportional to higher bulk density values. This is due to the addition of more dense red clay material and less porous and lightweight diatomite and rice hull ash materials in the composition.



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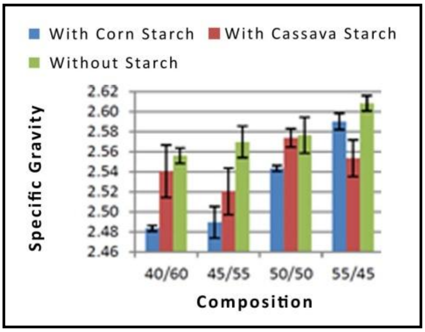


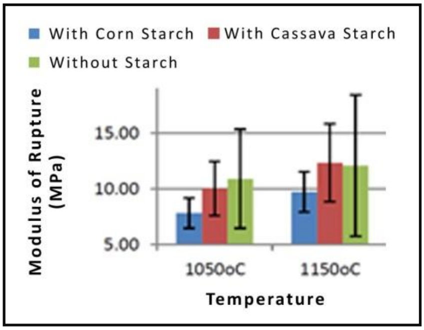
(b)

Figure 5. Effects of (a) temperature, and (b) composition in a specific gravity of the starch-containing and non-starch containing samples

3.6 Modulus of Rupture

A high modulus of rupture is favoured by increasing the temperature from 1050 to 1150^{o}C as illustrated in Figure 6. This is due to the elimination of some pores during densification which increases flexural strength.

Formulated bodies made by slip casting have high strength because of uniform packing of particles and pore spaces as the result of the forming process which during densification is brought even more close together through partial fusion. Moreover, higher clay content and lower silica results to higher values. In this study, clay works as a binder that supports the body as a whole and increases shrinkage and density, thus producing higher strength for the material.



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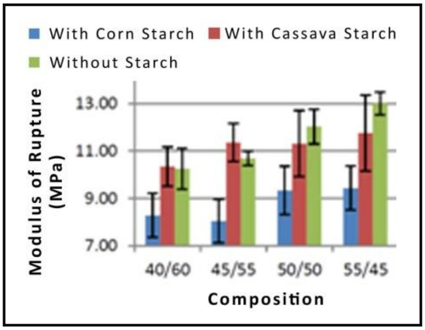

(b)

Figure 6. Effects of (a) temperature and (b) composition in the modulus ruptureof the starch-containing and non-starch containing samples

3.7 Microstructure

The SEM analysis displayed the overall fired morphology of the pore structure left by the starch particles and carbonates from diatomite after burning out of fired samples as shown in Figures 7 to 10. Furthermore, the pore size of the materials ranged from about 0.50 to 10 µm and the internal shape of the pores varied from circular to irregular sizes that also reveals broken cylindrical diatom frustules or silicon-rich perforated cell walls (Diatoms, 2008).

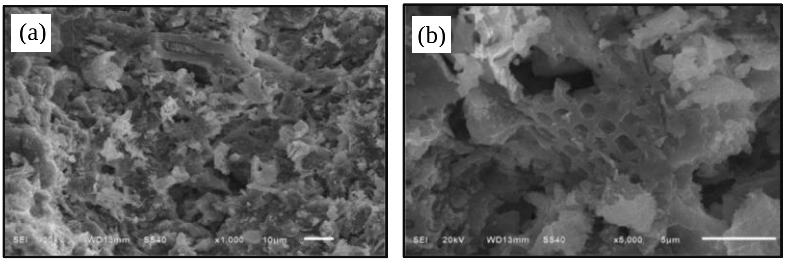

Figure 7. SEM images of fractured surfaces of SC6 (45C/55S-WCA) slip cast samples fired at 1050oC (a) x1000 (b) x5000 magnification

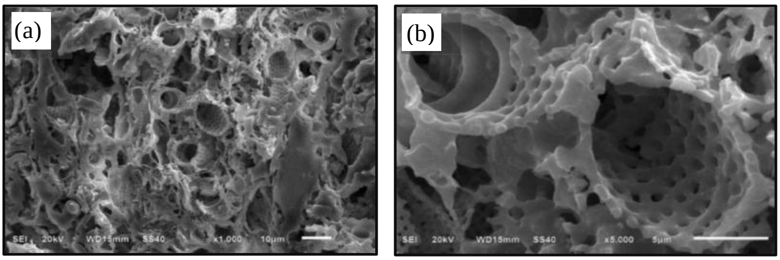

Figure 8. SEM images of fractured surfaces of SC6 (45C/55S-WCA) slip cast samples fired at 1150oC (a) x1000 (b) x5000 magnification

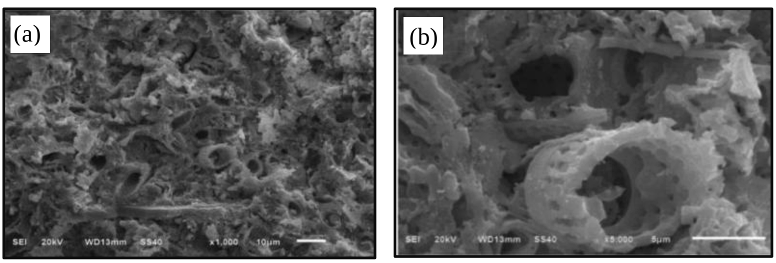

Figure 9. SEM images of fractured surfaces of SC12 (55C/45S-WOS) slip cast samples fired at 1050oC (a) x1000 (b) x5000 magnification

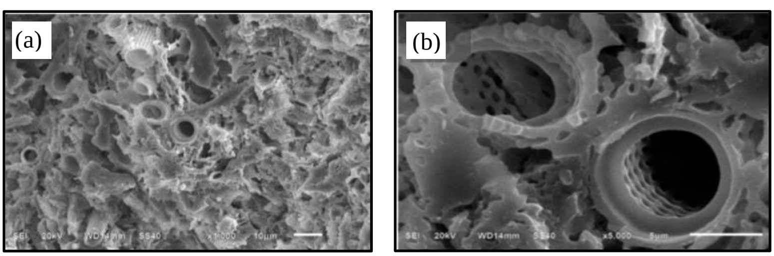

Figure 10. SEM images of fractured surfaces of SC12 (55C/45S-WOS) slip cast samples fired at 1150oC (a) x1000 (b) x5000 magnification

3.8 Elemental Analysis

The EDX analysis was performed on the same area used in the morphological study to investigate the composition as shown in Table 3. Results confirm the presence of perhaps silicon spinel $2Al_2O_3.3SiO_2$, silica-rich mullite $3Al_2O_3.2SiO_2$ and amorphous silica SiO_2 (Chen *et al.*, 2000) for samples fired at 1050°C and 1150°C, respectively. This is assuming the mullite stoichiometry of 3:2 mullite of having an Al_2O_3/SiO_2 ionic ratio of 3:1. However, there are reports of mullite phases with up to and greater than 9:1 Al_2O_3/SiO^2 ratios (Shackelford and Doremus, 2008). Meanwhile, other metallic elements such as sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), titanium (Ti), and iron (Fe) also presented as minor elements. Fe+ cation is noted as the major impurities as shown in and may be in the form of hematite (Fragoulis *et al.*, 2004; Sglavo *et al*., 2000).

Table 3. Atom percentage elemental analysis test result of fired examples

Sample No.	SC6-1050	SC6-1150	SC12-1050	SC12-1150
Si	42.46	40.47	45.57	45.46
Al	11.99	12.99	12.63	14.54
O	40.28	38.11	34.61	32.71
Fe	3.24	3.36	4.52	3.61
[Si]/[Al]	3.54	3.12	3.61	3.13
Al/Si	4:1	3:1	4:1	3:1
Si	42.46	40.47	45.57	45.46
Al	11.99	12.99	12.63	14.54

Legend: Si-silicon, Al-aluminum, O-oxygen, Fe-Iron; 1050 ^{0}Cand 1150 ^{0}C-firing temperature

3.9 Best Formulations

The best formulation for water aeration diffuser application is sample SC12 (SLC-55/45-WOS-1050). Table 4 shows the various data parameters of the physical, microstructure and chemical properties of sample SC12. It was also tested initially for bubble formation using an air pump with 20 watts power of 0.025 MPa pressure and fine bubbles were successfully formed in clear water set-up.

Table 4. Summary of the parameters of the best formulation

Parameters	SC12(SLC-55/45-WOS-1050)
Dry Shrinkage	9.50%
Fired shrinkage	9.15%
Total shrinkage	18.65%
Water Absorption	36.28%
Loss on Ignition	11.43%
Apparent Porosity	48.26%
Bulk Density	1. 33
Specific Gravity	2.57
Flexural Strength	18.11 MPa
Pore diameter	~0.5-10 μm
Parameters	SC12(SLC-55/45-WOS-1050)

Legend: SLC-slip casting; WOS- without starch; WCA-with cassava starch; 1050 ^{0}C and 1150 ^{0}C-firing temperature

4. Conclusions and Recommendations

Red clay-based porous ceramic for air diffuser applications was developed. The effects of the additives used, temperature, and composition to the physical properties of the porous ceramics were studied. The microstructure pore size is in the range of 0.50 to 10 μ, and the pore shape varies from irregular to circular with the presence of cylindrical diatom frustules. The chemical analysis confirms the mullite formation of samples made by dry pressing, slip casting and starch consolidation casting. The best formulation appropriate for air diffuser is formulation S12 that is produced by slip casting with composition of 55:45 clay to silica ratio or 55% Lama-Lama clay and 40% Kapatagan diatomite-5% RHA without starch and fired at 1050^{o}C.

Suggestions for further development of this study comprise the following: (1) conduct test for permeability characteristics determined from the gas pressure drop across the porous sample and the resulting gas flow rate; (2) subject the best formulation for oxygen transfer efficiency (OTE) using a water quality measurement device; (3) perform X-ray diffraction (XRD) analysis of the fired samples to identify the phases present in the samples; (4) conduct durability test of samples determined as the mass lost after treatment in 0.1M HCl and 0.1M Na_2CO_3 for 30 days; and (5) conduct actual field test for the porous ceramic diffuser for water aeration in a pond or lake system for comparison with a standard sample.

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