Original Research Article

INCORPORATING RICE HUSK ASH IN METAKAOLIN-BASED GEOPOLYMER BINDER.

Abstract

Geopolymers are interesting materials synthesised by activating aluminosilicate source(s) with alkaline activator(s). The activators often used for this purpose are alkali metals of silicates and hydroxides. Environmental impact assessment carried out on geopolymers however indicates adverse contribution of this process to several other environmental indices despite the reduction in CO_2 emission. Several biomass sources are known to possess a high silica content. This research investigates the effect of incorporating rice husk ash (RHA) in the production of geopolymers. 2g, 4g, 5g, 6g, 8g and 10g of RHA was introduced as a source of silica into the geopolymer binders. Sodium silicate to sodium hydroxide ratio of 0, 1 and 1.5 was used for the synthesis. From the compressive and flexural strength tests, increasing the RHA content improved the performance of the binders. Optimum compressive and flexural strength was gotten at 10 g (15.25 MPa) and 4 g (3.45 MPa) RHA content respectively. Binders produced with only SH solution and RHA showed a significant 95% increase in strength as the RHA content increased.

Keywords: Geopolymer, Metakaolin, Sodium Hydroxide, Rice Husk Ash, Sustainable Materials

1.0 Introduction

The synthesis of GPs basically requires a precursor and an activator, and the sources of these constituent materials vary widely [1, 2]. While the precursors may come from industrial/agricultural residues and rock-based materials, the activators are commonly sourced from alkali silicates and hydroxides of alkali metals of Na and K and sparsely sourced from alkali aluminates, carbonates and sulphates and even acid-based activators like phosphoric acid and aluminium phosphate-based activators [3, 4].

Geopolymers have shown to be good alternatives to ordinary Portland cement due to its lower CO_2 emission [5] but one set back with this product is its consumption of a large quantity of hydroxides and silicates during synthesis which has a negative effect on other environmental indices such as abiotic depletion, ozone layer depletion, human toxicity, fresh water ecotoxicity, marine ecotoxicity, acidification, eutrophication and terrestrial ecotoxicity [6]. There is thus a need to investigate methods of reducing or substituting the source of the alkaline silicate solution used given that it is reportedly a major contributor to the environmental indices of geopolymers. This will go a long way in making the technology more sustainable, renewable and acceptable

With utilising alkaline activators, apart from problems with handling, recent concerns have been raised, attributing a high environmental impact value to them especially with the silicates [5, 6]. Based on these reports, current research are directed towards investigating methods to reduce the negative effects this binder has on the environment with more focus on reducing the amount of synthetic activators and replacing them with more sustainable sources [2]. The contributing environmental indices of the silicate is reputed to be more than that of the any of the other activators, thus it has received more attention in terms of seeking alternative, environmentally friendly sources. Some researchers have attempted to incorporate silica in the mix by introducing materials such as silica fume, RHA, glass powder and sugar cane bagasse ash that have a high silica content of silica [7–9]. This research however, goes further to compare the effect of two increasing the silica content in the ash while reducing the amount of silica in the activator.

2.0 Experimental

2.1 Materials

The kaolin samples used for this research was extracted manually from a natural deposit in Markarfi, Kaduna State, Nigeria. The samples were homogenized, dried and filtered through a 200µm sieve in order to obtain a more uniform size, remove moisture and filter some large impurities. Rice husk ash was used primarily due to the high content of amorphous silica in it and also in an attempt to utilize waste materials generated during rice production The rice husk was also sourced locally from a rice processing mill in Ogoja, Cross River State, Nigeria. Impurities such as stones and straws were removed manually from the husk after which it was pulverised and burned in a muffle furnace at 600^{o}C. Liquid sodium silicate with 2.5 module (SiO_2/Na_2O) and analytical grade sodium hydroxide with 98% purity was procured at Ibra Hadad Nigeria Ltd, an authorized distributor of Honeywell Research Chemicals in Nigeria.

2.2 Characterisation of raw materials

The determination of the particle size distribution after preparation of the kaolin was done by sieve analysis with eight different sizes of sieves; 5µm, 10µm, 20µm, 30µm, 50µm, 75µm, 100µm, 150µm and 200µm. The chemical composition of the kaolin and rice husk samples were obtained through by carrying out x-ray fluorescence while the mineralogical composition was carried out by x-ray diffraction analysis through an Empyrean diffractometer system. XRD was performed with a CuKα radiation varying from 5^{o} to 75^{o}, 0.05^{o} 2θ step-scan and 1.0 s/step. Finer particle size distribution is a catalyst for geopolymerization and the particle size distribution of the materials is shown in Figure 1. The kaolin had an average particle size of 33.8µm while the MK (kaolin calcined at 700^{o}C) had an average particle size of 22.1µm. It can be observed from this result that the calcination aided in producing a finer particle size which can also improve the chemistry of reaction. RHA on the other hand had an average particle size of 8.2µm.

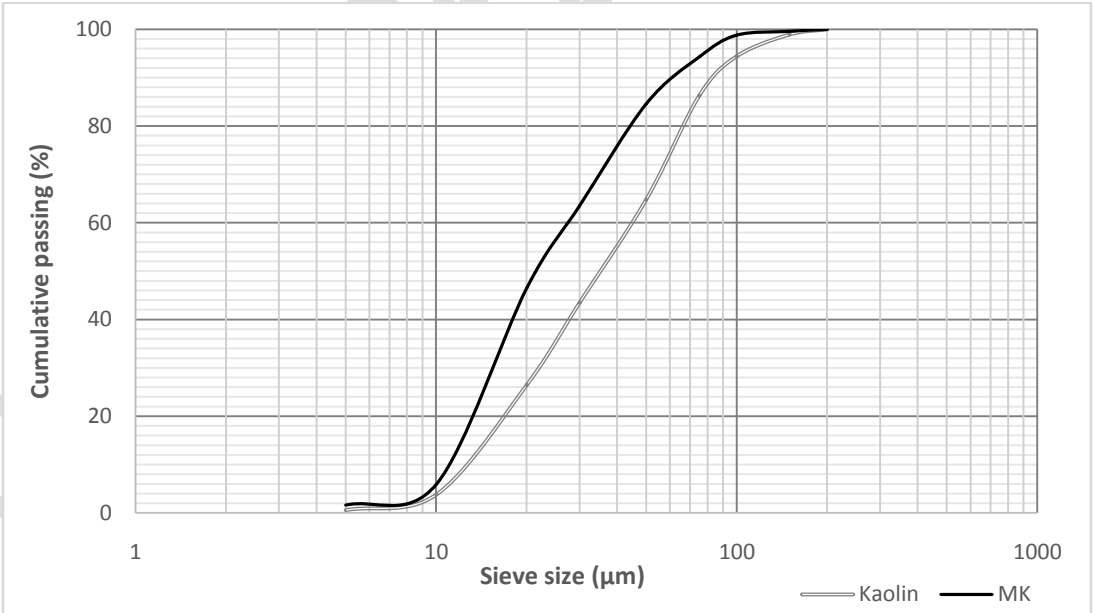

Figure 1: Particle size distribution of kaolin and metakaolin

2.3 Synthesis, Testing and Characterisation of Geopolymer Binders

A small quantity of the kaolin was taken from the extracted source for chemical analysis by means of x-ray spectroscopy and x-ray diffraction. Metakaolin was prepared by calcination of the kaolin in a

muffle furnace at a heating rate of 20^{o}C/min from 25^{o}C to 700^{o}C for 2 hours and the sample was also sent for x-ray spectroscopy analysis. A representative sample of the RHA was collected for chemical characterisation. The 10M concentrated NaOH solution was prepared by dissolving the right quantity of pellets with water and this was done at least 24 hours prior to usage. With the aim of determining the effect of reducing the silica content from the activator and increasing the RHA content, different Na_2SiO_3/NaOH (SS/SH) ratio of 0, 0.5 and 1.0 was investigated.

Table 1: Mix proportion of samples

S/N	RHA Content	SS/SH ratio	S/L	Density (g/cm^3)
1	0	0	1.2	2.08
2	0	0.5	1.2	2.12
3	0	1	1.2	2.18
4	2	0	1.2	1.98
5	2	0.5	1.2	2.05
6	2	1	1.2	2.07
7	4	0	1.2	1.87
8	4	0.5	1.2	1.92
9	4	1	1.2	1.93
10	6	0	1.2	1.80
11	6	0.5	1.2	1.83
12	6	1	1.2	1.87
13	8	0	1.2	1.84
14	8	0.5	1.2	1.84
15	8	1	1.2	1.85
16	10	0	1.2	1.81
17	10	0.5	1.2	1.83
18	10	1	1.2	1.85

Minitab software was used to develop factorial design of experiments for two quantitative factors – RHA content and SS/SH ratio – with six and three levels respectively. The experimental design was completely randomized and eighteen (18) mix proportions were developed with three replicates (Table 1).

Two-part mixing method was used to prepare the geopolymer binders. The solid samples (RHA and metakaolin) were measured in the required quantity and mixed while the liquid samples (SS and SH) were also measured based on their ratios. A precursor (solid) to activator (liquid) (S/L) ratio of 1.2 was used to prepare all samples. This was the most suitable ratio obtained after conducting various test mixtures because it had the best consistency and flow. In producing the GP binder, the alkaline solution was poured into a measured quantity of the MK and mixed at a low velocity (190rpm) for 2 mins and at a higher velocity (210rpm) for 3 mins before finally mixing at low velocity for another 3 mins. The final binder was then poured in a silicone mould of size 50mm x 50mm x 250mm, vibrated for 5 mins to remove air bubbles and allowed to cure at ambient temperature for 28 days. Subsequently, the samples were subjected to compressive and flexural testing when they attain their curing time according to the ASTM C109 and ASTM C293 respectively. Samples for compressive test were cut to cubic size of 50mm x 50mm x 50mm. Once the specimen was fractured, the pieces were preserved in an air tight zipper bag.

Minitab software was use to statistically analyse the results after imputing the response (compressive and flexural strength). The aim of this analysis was to get a correlation between the factors and the

responses received and to determine the optimal levels of each one. Pareto charts were also presented to provide a better understanding from the ANOVA analysis. This chart shows the contributing effect of each factor to the response, in this instance the responses are the flexural and compressive strength. This chart has a reference line that indicates the statistical significance of each term with a t-level associated to the null hypothesis for $\alpha = 0.05$ (5% significance level)

3.0 Results and Discussion

3.1 Kaolinite characterisation

Table 2 shows the chemical composition of the kaolin and RHA. The kaolin is basically composed of silica (51.18) and alumina (32.35) with a silica to alumina ratio of 2.69. The total content of the SiO_2 and Al_2O_3 in the kaolinite is approximately 84% which is typical of most aluminosilicate sources [12], [13]. The diffractogram of the raw clay show mainly kaolinite with little content of muscovite. Comparing the XRD patterns of the raw and calcined kaolin, diminishing patterns of the peaks of the kaolin are visible and this is because the calcination produces a more amorphous structure which will make the precursor more reactive (Figure 2).

RHA had a larger content of silica (76.49) and smaller amount of CaO (2.87), Al_2O_3 (4.75) and Fe_2O_3 (3.11). Several other research have recorded an even higher content of silica in RHA above 90 % [14] and this significant content of silica is what makes it suitable for being used as an alternative to the silicate activator.

Table 2: XRF analysis of kaolin and RHA

Raw Material	**Chemical Composition**										
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	K_2O	MgO	Na_2O	CuO	Others	LOI
Kaolin	51.18	32.35	0.34	0.88	0.02	1.87	0.01	0.01	0.25	1.03	12.06
RHA	76.49	4.75	3.11	0.22	2.87	1.41	2.37	0.01	0.02	2.25	6.5

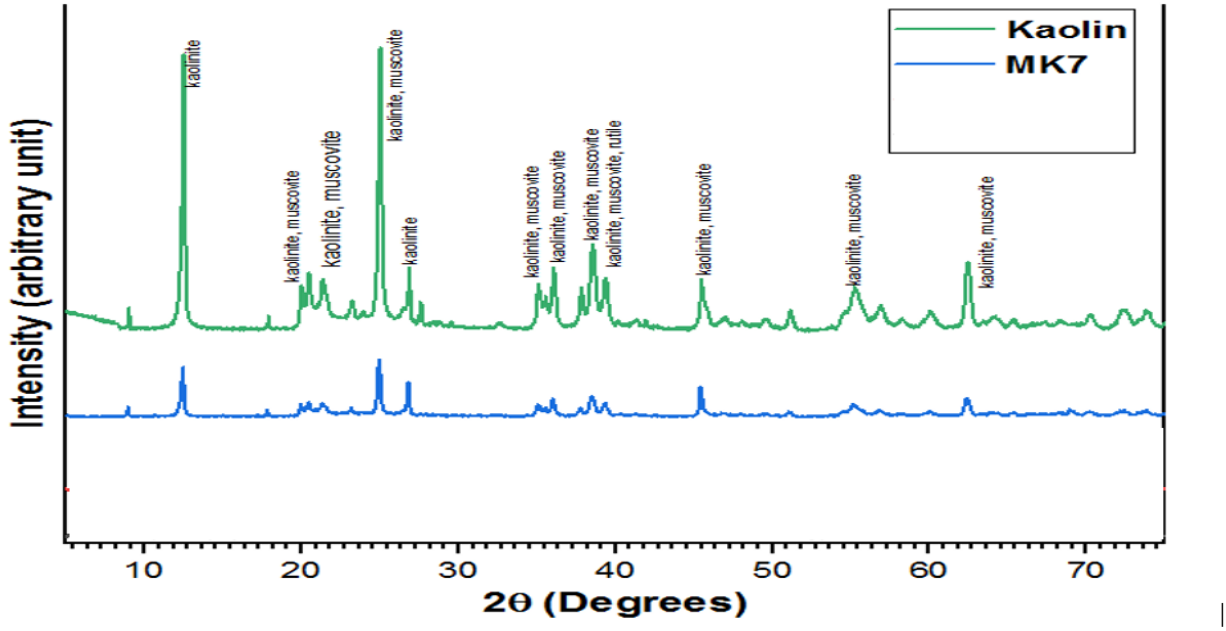

Figure 2: XRD pattern of raw kaolin and calcined kaolin (700^oC)

3.2 Effect of RHA content on the compressive strength of geopolymer binder

Figure 3 depicts the compressive test result of the metakaolin-based geopolymer binder reinforced with RHA at different weight percent and at different SS/SH ratio. Generally, binders produced with only

SH solution (SS/SH at 0) produced lower compressive strength but the strength increased from 5.2 MPa to 9.5 MPa with the introduction of the RHA to 10 g. Geopolymer binders produced with SS/SH ratio of 1 had the best performance of 15.25 MPa at 8 MPa while those with SS/SH ratio of 0.5 had a comparable strength of 14.75 MPa.

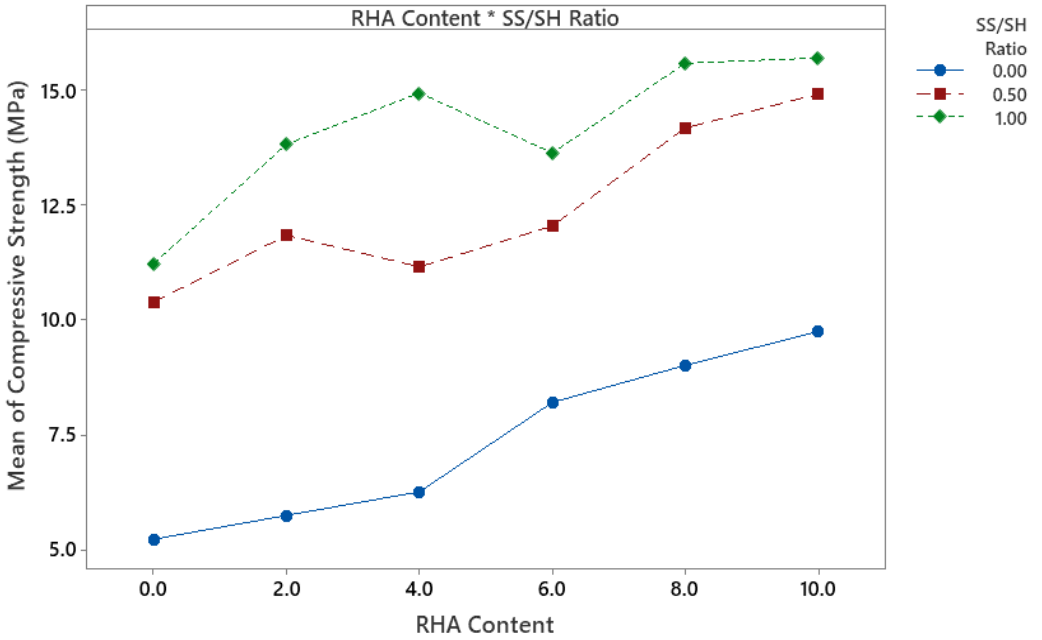

Figure 3: Interaction plot for compressive strength

The addition of the RHA in the mix in significant quantity (6g, 8g and 10g) increased significantly by about 80%. Below 6g weight percent of RHA, the ash had no significant contribution to the compressive strength of the geopolymer binder. In some research, it is reported that the increase in fibre/ash content above a particular percentage can lead to a decrease in strength [15]. This however was not observed in this research as the highest strength was obtained at the highest ash content (10 g weight of ash). This may be most likely due to the final particle size of the RHA compared with when fibres are being used. The result obtained suggests that the sodium silicate content can be reduced and ash introduced to give similar properties with those produces with higher synthetic sodium silicate content.

3.3 Effect of RHA content and SS/SH ratio on the flexural strength of geopolymer binders

Figure 3 shows the flexural test result of the metakaolin-based geopolymer binder reinforced with RHA at different weight percent and at different SS/SH ratio. Similar to the compressive test results, binders produced with only SH solution produced lower flexural strength but the strength increased from 1.5 MPa to 2.6 MPa with the introduction of the RHA to 10 g weight. Geopolymer binders produced with SS/SH ratio of 1 had the best performance of 3.45 MPa at the 4 g weight of RHA. A slight decrease in the flexural strength was obtained from the 6 g weight of RHA and the strength remain similar till the 10 g weight RHA. The results obtained here is similar to those obtained from the compressive strength. The flexural strength increased with increase in SS/SH ratio and RHA content. Reducing the content of sodium silicate and increasing the content of the RHA can give similar strength.

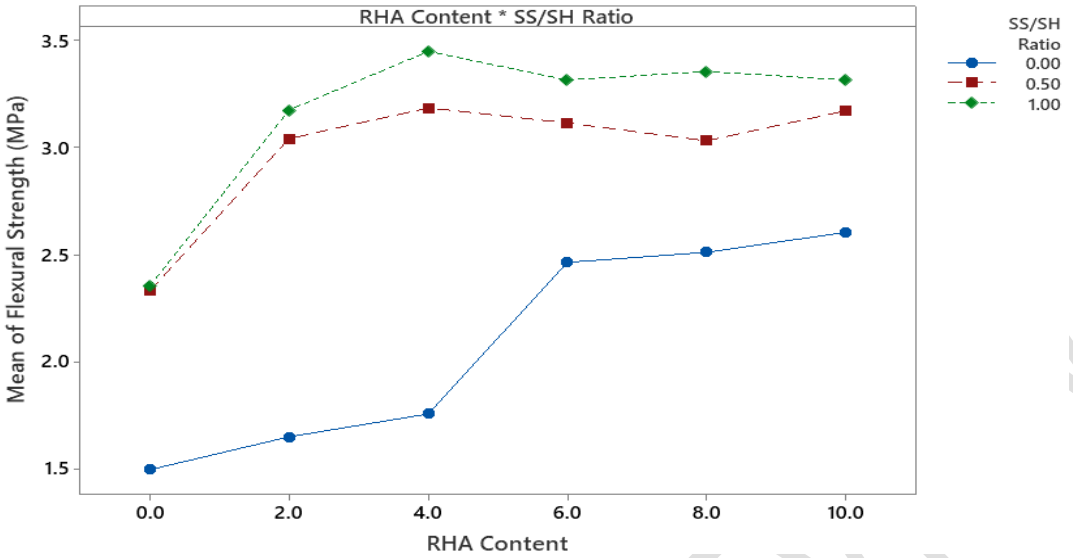

Figure 4: Interaction plot for flexural strength

3.4 Effect of RHA content and SS/SH ratio on the compressive and flexural strength of the geopolymer binder

The pareto chart attempts to describe the effect of the factors (RHA content and SS/SH ratio) on the responses (compressive and flexural strength) for the geopolymer binders. The factors beyond the dotted line means that the factors were significant at the 95% confidence level. Considering Figure 5, the RHA content and SS/SH ratio contributed significantly to the compressive strength of the geopolymer binders. The combined effect of the factors however did not contribute significantly to the strength of the binders. Similarly, the pareto chart for the flexural strength depicts a significant contribution from both factors; RHA content and SS/SH ratio. Unlike the compressive strength, combined effect of the factors on the flexural strength, got beyond the 95% significant level.

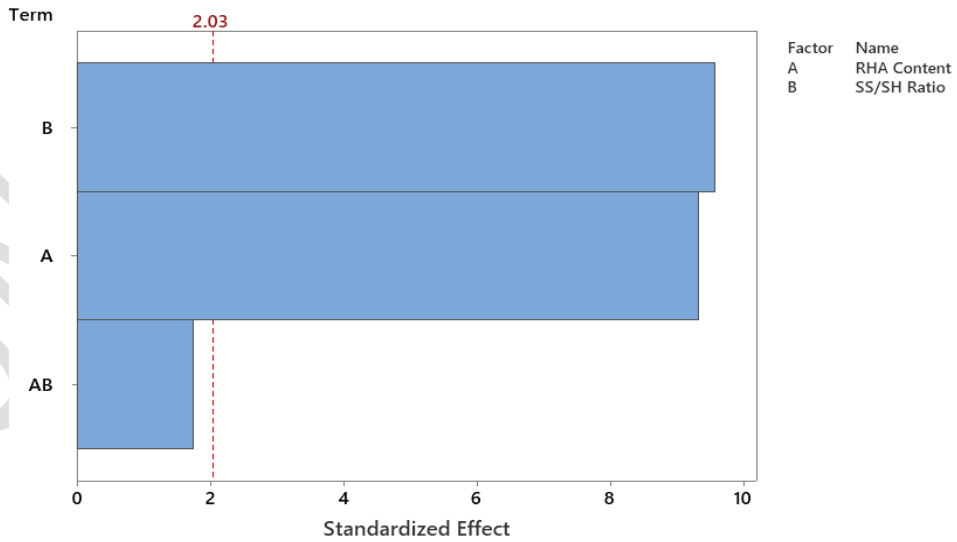

Figure 5: Pareto chart for compressive strength

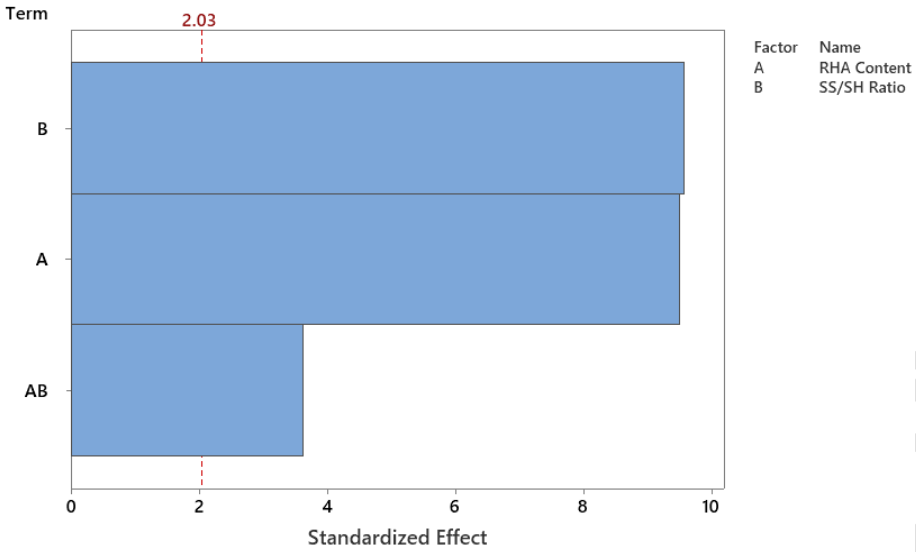

Figure 6: Pareto chart for flexural strength

4.0 Conclusion

This research investigated the effect of incorporating RHA (2g, 4g, 6g, 8g, 10g) in the synthesis of geopolymers in an attempt to reduce the use of synthetic alkali silicate solution and produce more sustainable binders suitable for construction industries. In this study, three SS/SH ratio of 0, 0.5 and 1 were investigated for five different RHA content by weight using the two-part mixing process and cured at ambient temperature for 28 days. The following are the main findings deduced from this study;

i. Increasing the RHA content from 2g to 10g in the geopolymer binders resulted in a constant increase in the compressive strength for all SS/SH ratios (0, 0.5, 1.0) investigated.
ii. Increasing the weight percent of the fibres in the mix resulted in a decrease in the bulk density of the binders from 2.18g/cm^3 to 1.85g/cm^3
iii. The Pareto chart shows that both factors (RHA content and SS/SH ratio) have more than 95% level of significance on the mechanical properties of the binders.
iv. The optimum RHA content that favoured the compressive strength was 10g (15.25 MPa) while an optimum for flexural strength was obtained at the 4g (3.45 MPa) weight of RHA. It is also worthy to note that reducing the optimum SS/SH ratio by 0.5 and incorporating 10g RHA produced a compressive strength of 14.75 MPa.

Data availability

The data used to support the findings are available from the corresponding author upon request

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