

Performance Evaluation of Cashew Nutshell Ash Aiming Their Use in Cement Composites

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Abstract

Every year, the agro-industrial sector generates a lot of waste by-products that, due to poor management and a lack of awareness of their values, present risks to the environment, society, and economy. One of the promising substitute materials for cement that can be used in the construction industry is cashew nut shell waste. Thus, the ash from cashew nutshell was investigated in this work. Since they are a byproduct of the energy generation process, ashes maintain a significant position among the agro-industrial wastes. Because most ashes include pozzolanic activity, they can be utilized in place of cement to create low-cost composites with less energy waste. The current study uses Thermogravimetric analysis (TGA), and differential thermogravimetric analysis (DTGA), X-Ray Fluorescence Analysis (XRF) and X-Ray diffraction (XRD). It is concluded that using CNSA in concrete is beneficial in reducing environmental and sustainability issues. CNSA concrete is advantageous in environments with high sulfate concentration. It was found that the total amount of silicon oxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) obtained in CNSA. An amorphous structure is indicated by the broadened peak that occurs in the XRD pattern at about $2\theta=24^\circ$. Increasing the activation temperature tends to cause the activated carbon to graphitize. Chemical testing revealed a low silicon (SiO_2) content, and the analysis of the CNSA-soluble extract revealed the presence of heavy metals.

Keywords: Cashew nut ashes; Agroindustrial waste; X-Ray diffraction; X-Ray Fluorescence Analysis; Thermogravimetric analysis

1. INTRODUCTION

The primary source of building materials is concrete. It would continue to be significant for future generations even with the advancements in human capabilities in construction technologies [1]. Cement manufacturing is rising to fulfill the demands of the world's expanding population, which raises greenhouse gas emissions like carbon dioxide (CO_2). The third most developed industry, cement manufacture, is accountable for the development of CO_2 , which is released 8–10% [2] for every ton of cement produced. The utilization of agricultural wastes as raw materials for concrete production is taken into consideration in an effort to reduce or eliminate the concrete industry's detrimental environmental effects and to advance the industry's environmental sustainability [3]. To minimize the use of cement in concrete, a few steps must be taken to reduce CO_2 production during the concrete manufacturing process, such as significantly lowering CO_2 transmission and raising the proportion of mineral admixtures. Concrete materials are partially replaced in order to attain sustainability. As a result, inexpensive and readily accessible elements are typically utilized as additives in concrete. For partial replacements in concrete with cementitious qualities, different researchers have employed pozzolanic materials.

Without sacrificing the concrete's quality and performance under applied loading conditions, a concrete mix is optimized to lower the costs of the constituents and the time spent conducting concrete trial mixes. The main ingredients of concrete (composite material) are aggregates and cement paste. While the water/cement ratio determines the quality of the necessary cement paste, the kinds, voids, forms, and surface area of the aggregates determine the amount of cement paste needed to achieve the desired concrete strength and quality. The key levels of mix parameters can be adjusted to optimize a concrete mix, as shown in earlier research.

Cement, aggregates, water, and occasionally admixtures to affect its fresh or hardened qualities make up the versatile building material known as concrete. In order to create a paste and bond the aggregates, Portland limestone cement (PLC) combines with water. When making concrete, cement serves as a

binder. It is a material that binds, hardens, and sets other materials. Although Portland limestone cement is used extensively and is the second-largest material used in construction after water, the process of making it releases carbon dioxide (CO₂) into the environment. However, it is hard to overestimate the increasing awareness and efforts to conserve natural resources and the environment in order to reduce CO₂ emissions through the influence of PLC production by the 2030 Sustainable Development Goals agenda [4]. In order to partially and fully replace PLC in the manufacturing of concrete, supplementary cementitious materials (SCMs), also known as agro-industrial wastes, such as fly ash, powdered granulated blast furnace slag, corncob ash, and rice husk ash, have been employed extensively. Therefore, the financial and environmental hazards associated with PLC can be reduced by employing pozzolanic agro-industrial wastes. But as a waste by-product, cashew nutshells are produced by the majority of processing enterprises and are carelessly disposed of or burned [5]. To put it simply, cashew nutshells are agricultural trash that contribute significantly to land and environmental damage in regions where they are grown or processed but not used.

Concerns about climate change and resource shortages around the world have fueled the need to create sustainable and eco-friendly materials in recent years. Because of this, researchers are now looking into composite materials that contain bioreinforcements like natural fibers (Iyyadurai et al., 2023a). The eco-friendliness of natural fiber reinforcing is one of its main benefits. Natural fibers are biodegradable and have a much smaller environmental impact throughout the course of their life cycle than synthetic fibers [6]. This is in line with the desire to lessen the carbon footprint connected to industrial processes and the increasing emphasis on sustainable practices around the world. Additionally, natural fibers provide outstanding particular qualities like low density, exceptional thermal insulation, and a high strength-to-weight ratio.

Cashews (*Anacardium Occidentale*) are a by-product of agriculture, with an estimated global production of 4,430,341 metric tonnes (MT), 4,087,563 MT, and 3,971,046 MT in 2015, 2016, and 2017, respectively [7]. The cashew, or *Anacardium occidentale*, is a cash crop that is grown in Central America, Brazil, Vietnam, India, and Nigeria. It is projected that Nigeria produces 636,000 metric tons (MT) of cashew nuts annually, according to the United Nations Food and Agriculture Organization. Nigeria, on the other hand, produced 97,149 MT, 98,291 MT, and 98,253 MT in 2015, 2016, and 2017. The production of cashews in the West African region increased by almost 12% year between 2005 and 2014 [8]. With over 1,350,000 MT, the West African region has surpassed Asian nations (India, Vietnam, Cambodia, and Indonesia) in production of cashew nuts, making it the world's largest producer. About 30 to 35 weight percent of cashew nutshell is oil, which is known as cashew nut shell liquid [9]. Additionally, 2,500,000 MT of cashew nuts are produced, resulting in roughly 1,825,000 MT of waste [10]. Nevertheless, it is unsettling to see how carelessly these wastes are disposed of, which degrades the ecosystem.

The cashew crop is grown on 8, 54,000 hectares in Tamilnadu, India, with an annual production of 7, 00,000 tons and a typical productivity of 710 kg/ha [11]. Among the cashew-growing regions in the state, the Cuddalore region has the highest cashew efficiency at 810 kg/ha and ranks first in cashew formulation with 24,302 tons [12]. With 3799 handling facilities, including 1850 small-scale cashew processing businesses, India is becoming the world's largest cashew processor [38]. The states that produce the most cashew nuts are in India [13]. To remove the oil that is present in the cashew nutshell, 70–75% of its weight is delivered to an oil extraction factory. For carbon composite materials, cashew nut shell liquid (CNSL) is used as a gum. Cashew Nut Shell Cake (CNSC) is the end product of extracting oil from cashew kernels. CNSCs are utilized as free igniters in incinerators because they still contain some oil after oil extraction. Two methods are used to transform the CNSC into Cashew Nut Shell Ash (CNSA): open burning and high-temperature burning in a mufe furnace. The flowchart for the CNSA generating process is shown in Figure 1.



Figure 1: Process of obtaining the CNSA [14]

2. LITERATURE REVIEW

Numerous advanced and waste materials, such as fy ash [15], silica fume [16], impact heater cinder, metal scrap, tire debris [17, 18], fibers, municipal solid waste incineration [19], rice straw ash [20], natural volcanic ash [21], glass powder [22], and so on. An important evergreen tropical crop is cashew. For environmental benefits, using total recycled concrete aggregates (TRCA) in concrete is the way to go. Studies by Oliveira et al. [23] and Grdic et al. [24] showed that TRCA addition in SCC marginally decreased mechanical and rheological characteristics. However, TRCA addition significantly increases the compressive, tensile, and shear strength of SCC, according to studies by Fakitsas et al. [24] and Khodair and Bommareddy [26]. It illustrates the intricate behavior of TRCA in SCC and is dependent on TRCA properties that depend on adhere mortar quality and content or TRCA treatment. To date, a number of treatment techniques have been used to improve the adhere mortar's qualities or decrease its thickness around the TRCA. To remove adherent mortar from TRCA, many techniques were used, including mechanical grinding, selective heat grinding. At the age of the 28-day curing period, it was identified that adaption of these physical treatments was successful in imparting 7% greater mechanical qualities. However, the TRCA hardness, texture, and bonding properties that were required to address the durability aspects of concrete are challenged by these processes.

Dai et al. [27] optimized the mix proportions for cement paste backfill materials. According to reports, the RSM might anticipate the feasibility of using industrial standard backfilling materials. Bahri et al. [28] also optimized the mix proportions of high strength-performance concrete treated with rice husk ash (RHA). The statistical results showed that the response models considerably fit to anticipate the mix variables and accurately optimized the responses, compressive strength. Furthermore, Liu et al. [29] used BBD in an effort to maximize the alkali-slag concrete (ASC) under freeze-thaw cycles. The findings showed that the independent variables—solutions ratio, slag concentration, and curing age—were well fitted. The response models can be used to determine the alkali-slag concrete's fracture toughness. RSM was also used to optimize a concrete that had been changed to include limestone filler. There is currently no research on optimizing a concrete mix that incorporates cashew nut shell ash (CNA), despite earlier work on optimizing concrete mixtures. The use of SCMs in the manufacturing of concrete lowers the costs, energy usage, and environmental effects of the constituents, promoting sustainable development and products as well as energy and environmental preservation. The durability characteristics and reactivity indices of geopolymer concrete (GPC) were examined by Oyebisi et al. [30], who used corn cob ash (CCA) and ground granulated blast furnace slag (GGBFS) as SCMs. The findings showed that the oxide compositions of GGBFS and CCA improved the GPC's reactivity, compressive strength, and chemical resistance. The impact of corncob ash on the geotechnical characteristics of lateritic soil stabilized with Portland cement was investigated by Akinwumi and Aidomojie [31]. The findings demonstrated that adding CCA to the

soil generally decreased its permeability, swell potential, and plasticity. It strengthened the soil as well. In addition to being more cost-effective and environmentally friendly than cement stabilization, CCA enhanced the soil's geotechnical qualities for the application of pavement layer material. The necessary energy and material costs are reduced by roughly 20–67% and 33–80%, respectively, with 25–50% of SCMs by weight percentage of cement. Because some SCMs are used more widely, CNA is rarely used as an SCM in the manufacturing of concrete. One byproduct of agricultural products is cashew nutshell. Nigeria produced roughly 0.1 million metric tonnes (MMT) of the approximately 4.5 MMT produced worldwide in 2017. Approximately 1.825 MMT of waste is produced from the production of 2.5 MMT of cashew nuts.

Investigation on the use of CNSA as a building material in civil engineering application is still few or nonexistent. Pandi and Ganesan [32] investigated the sorptivity and water absorption of PC concrete that was moderately substituted with CNSA. When PC concrete was substituted with 25% CNSA, it was discovered to exhibit reduced water absorption and sorptivity than normal concrete. In a related study, Pandi et al. [33] looked at how best to use CNSA in the manufacturing of concrete. The results showed that CNSA, which replaced 25% of PC, resisted higher axial and bending loads as well as permeability than ordinary concrete. Additionally, Thirumurugan et al. [34] investigated the strength characteristics of concrete that has been partially substituted with CNSA. The findings showed that a 20% substitution of CNSA for PLC enhanced the strength of the concrete with a 0.45 water-to-cement ratio. Similar to this, Pandi and Ganesan [35] looked at the mortar's sorptivity and water absorption when it included CNSA. It was discovered that CNSA mortar with a 1:3 mix had a higher water absorption than conventional mortar and a lower sorptivity than conventional mortar. However, the physical and chemical examination of CNSA as a cement composite was investigated by Araujo et al. [36]. Chemical testing revealed that the CNSA had a low silicon oxide (SiO_2) content, which limited its use as a pozzolanic ingredient in blended cement. Concrete's fresh and hardened qualities are enhanced by these two CCNA variations (SiO_2 -based CCNA and CaO-based CCNA). Because of the low quantification or lack of CaO, SiO_2 -based CCNA with ordinary portland cement (OPC) improves the slump factor and compaction factor qualities, suggesting retarder behavior in cement paste in the first state of hydration. Because high quantifiable CaO speeds up the cement paste's hydration process, CaO-based CCNA imparts a reducing nature in slump flow performances. Comparing calcined and uncalcined agro-waste products for use in concrete applications has been the subject of a few research.

3. MATERIALS AND SAMPLE PREPARATION

3.1 Material Selection

India is one of the world's largest cashew nut growers. Of these, 710 kg/ha of cashew nut cultivation is contributed by Tamil Nadu alone. Based on these facts, the Tamil Nadu government and the Indian government may face difficulties in disposing of the cashew nutshell. A portion of the cashew nutshell was used to extract gum for carbon composite materials, and approximately 75% of the total was used to extract oil. Cashew nutshell, which may include a little amount of oil, is made by compressing the remnants left over after the oil extraction process. It is typically burned or passed through a muffle furnace to produce biochar before being dumped in the ground, which can seriously pollute the environment and reduce soil fertility. According to research on the ash, the presence of certain elements is thought to enhance the material's mechanical characteristics and attributes more when it is utilized as reinforcement.

3.2 Sample preparation

The raw material was cashew nut shell trash that was gathered from Madurai, Tamil Nadu. Cashew nutshell trash is a form of agricultural waste that can be turned into biochar using a slow pyrolysis process. The basic components are separated from the cashew nutshell waste by hand. Following the removal of the cashew nuts, the shell residue is gathered and allowed to dry in the sun to eliminate any remaining moisture. A crop sun drier was used to dry the nuts for three weeks, and then the shells were taken off. The shells were crushed using a GS 160 grinding machine after being further dried for two more weeks with the same solar crop drier. After that, the gathered trash was firmly packed into a small container that was carefully sealed to keep out air. After that, the canisters are carefully put inside the furnace and heated continuously for an hour until they turn to ash.

4. METHODOLOGY

4.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a useful technique for evaluating a material's thermal behavior over a wide temperature range. The stability, purity, and temperature tolerance of a variety of materials, including polymers, fuels, and fibers, are assessed using this analysis technique. Because of this, TGA is especially helpful for analyzing novel biobased products and materials and contrasting them with the biobased and non-biobased alternatives that are currently available on the market. A sample's weight is measured during thermogravimetric analysis as the temperature it is subjected to rises. Although we may perform this study in a variety of atmospheres, the most popular ones are air and nitrogen.

In the current study, the thermal breakdown and weight loss of the cashew nutshell ash (CNSA) samples are investigated using thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA). A Mettler Toledo TGA apparatus, which precisely records changes in a sample's mass at the microgram level throughout a regulated heating process, was used to perform thermogravimetric analysis. The Cashew nutshell ash samples were carefully processed to minimize any possible restrictions on internal heat and mass transmission.

Samples weighing less than 10 mg were utilized in the test. Nitrogen was employed as an inert carrier gas and heated at a rate of 10°C per minute for the thermogravimetric investigations. The range of temperatures used was 25°C to 500 °C. Figure 2 shows the TGA instrument.



Figure 2: The thermogravimetric analysis (TGA) instrument

4.2 X-Ray Fluorescence Analysis (XRF)

Analysis of Cashew Nut Shell Ash (CNSA) using X-Ray Fluorescence. Twenty grams (20g) of CNSA were oven-dried for one hour at 100°C and then allowed to cool outdoors. A binder was added to the ash in a ratio of 1g cellulose flakes to 5g CNSA. An XRF, model ARL 9400XP+ Thermo, Switzerland, was used to measure the elemental concentrations of cashew particles after it had been set up for two hours to warm up. Soon after, the average concentration of each element was determined, and the proper energy band values were chosen. The XRF analysis of CNSA revealed elements such as copper, zinc, potassium, magnesium, sodium, iron, manganese, phosphorus, lead, and calcium. Because of the loss during igniting, the total mass percentage is not equal to 100.

4.3 X-Ray diffraction (XRD)

The objective was to determine which materials were mostly crystalline and to look for ash in the amorphous phase. As seen in the Figure 3, an XRD was performed using a Panalytical model called X'pert Pro. The following requirements have to be met in order to conduct the analysis: Cu K α radiation; 45KV voltage; 100mA current; 0.02° 2 θ scanning step; 2°/min scanning duration; and 3 to 100° (2 θ) scanning intervals. The formula used to calculate the crystalline index (Crl).

$$\text{CrI} = \frac{I_{200} - I_{am}}{I_{200}} \times 100$$

where I_{am} is the intensity of the diffraction at $2\theta = 12.2881$ and I_{200} is the maximum intensity of the diffraction at 200 peaks ($2\theta = 22.248$).



Figure 3: X-Ray diffraction (XRD) instrument

5. RESULTS AND DISCUSSION

5.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis creates a curve that shows how temperature (or time), represented on the x-axis, affects the sample weight, represented on the y-axis. The weight is usually expressed as the proportion of the sample that remains at a given temperature and time. Additionally, our reports contain a second y-axis on the graph that shows the data for the first derivative of the TGA curve. The mass loss percentage per degree Celsius or mass loss percentage per second are two examples of how rapidly mass changes in response to temperature and time, respectively, as seen by the Derivative Thermogravimetric (DTG) curve. Visual evaluation of the data is often facilitated by the DTG curve since it makes times of considerable mass change simpler to see. The relative abundance of the various chemical components in the sample can be inferred from the mass losses at particular temperature ranges. When nitrogen is used as the ambient gas instead, the resolution of the analysis often increases and the temperature ranges tend to move upward. A steady weight drop may indicate the presence of multiple volatile components in the environment, while a quick weight decline usually shows the abundance of one component.

Thermal decomposition profile (TG) and differential thermalgravimetric (DTG) curves were the thermogravimetric outputs of the TGA program. Figure 4 displays the results of the thermal decomposition analysis that TGA conducted. Drying, devolatilization, and residues (char and ash) are the three primary zones where weight loss is dispersed, according to the TGA profile. An initial process that results in the loss of water molecules between 25°C and 105°C that causes the 1.35 weight percent. Temperatures below 110°C caused the moisture content to drop by 3.76% of the sample weight.

The labile functional groups created during the oxidation process in the form of CO₂ and CO are broken down and eliminated during the second thermal breakdown process, which occurs between 100°C and 300°C. This results in a weight loss of 1.99% and is attributed to devolatilization [8]. There is a 0.23 % weight loss during the third thermal breakdown stage, which occurs between 380°C and 500°C. According to the TGA, the overall decomposition is 2.46%.

There are four peaks on the DTG curve for weight loss steps. The first phase takes into consideration the elimination of moisture, which peaks around 110°C. The second significant weight loss stage is the breakdown of hemicellulose, which took place between 190 °C and 260 °C. The DTG curve's inflection point indicates that the largest amount of hemicellulose was removed at 260 °C. The third step of weight loss, which is for the breakdown of cellulose, occurred between 260°C and 420°C and peaking at 310°C. After 420°C, the rate of decomposition was nearly insignificant, which corresponded to the char components' deformation into ash.

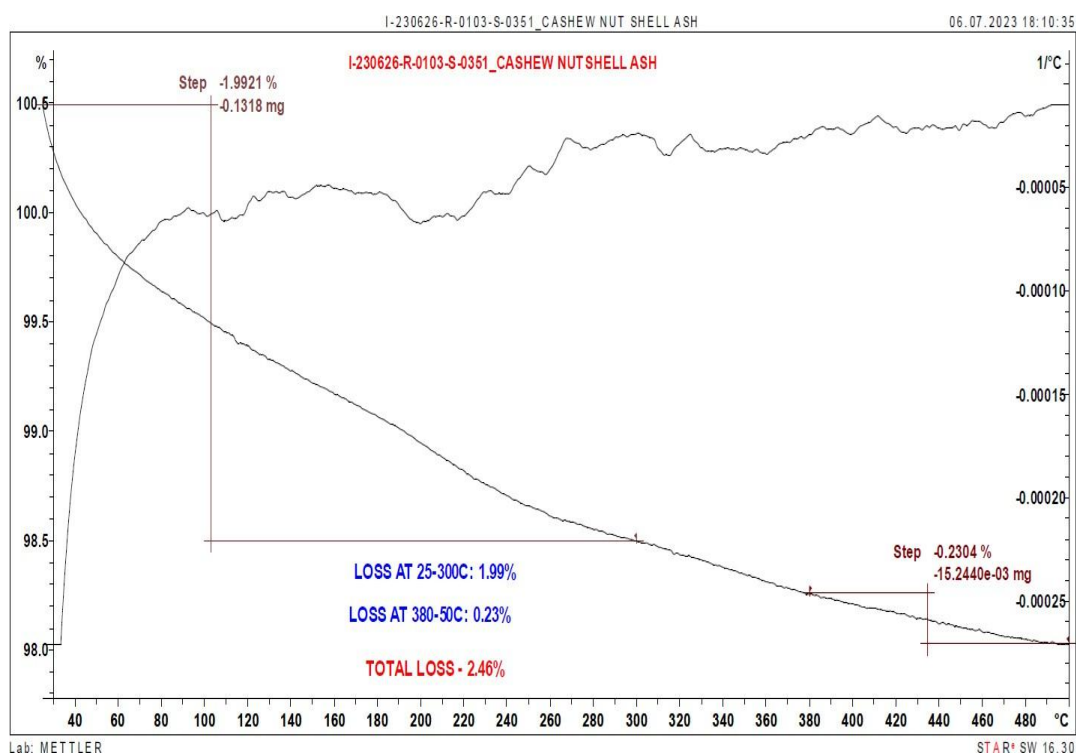


Figure 4: (TG) and (DTG) curves of cashewnut shell ash

5.2 X-Ray Fluorescence Analysis (XRF)

The XRF analysis is used to determine the chemical composition. The composition of CNSA as revealed by XRF analysis is displayed in Table 1. Cashewnut shell ash has been shown to have a large amount of magnesium oxide (25.858%), silicon dioxide (24.33%), potassium oxide (12.974), calcium oxide (11.815), and ferric oxide (8.071%). In the CNSA, the combined chemical composition of SiO₂+ Al₂O₃+ Fe₂O₃ is 33.98%, which is higher than the OPC (27.70%) in the study by Olubajo et al. [37], and 28.9% in the study by Afolayan et al. [38].

Table 1: X-Ray Fluorescence analysis result on cashew nut shell ash.

Parameters	Cashew nut shell ash Composition (%)
LOI	6.85
Na ₂ O	0.691
MgO	25.858
Al ₂ O ₃	1.615
SiO ₂	24.303
P ₂ O ₅	5.574
So ₃	0.324
Cl	0.04
K ₂ O	12.974
CaO	11.815
TiO ₂	0.455
Cr ₂ O ₃	0.038
MnO	0.899
Fe ₂ O ₃	8.071
SrO`	0.107
ZrO ₂	0.078
BaO	0.158

5.3 XRD Analysis

Using the primary compounds found in the XRF analysis, a screening was carried out following background definition, curve smoothing, and peak identification. This method was used to the ash sample taken from the shell of a ceshew nut.

The crystallinity of the ceshew nut shell ash shown in Table 2. The crystallinity of the ceshew nut shell ash produced is similar to the crystalline index for corn husk reported. Protoenstatite ($MgSiO_3$), potassium silicate ($K_2Si_4O_9$), calcium iron silicate ($CaFeSi_2O_6$), and magnesium oxide/periclase (MgO) have been found to have the highest crystallinity index, after quartz (SiO_2).

Table 2: Quantification (wt %) results of the ceshew nut shell ash.

Crystalline Phase	S-0034
Calcium Hydroxide/ portlandite ($Ca(OH)_2$)	-
Magnesium Oxide/ periclase (MgO)	7.0
Calcium Magnesium Silicate ($Ca_2Mg(Si_2O_7)$)	-
Quartz (SiO_2)	55.2
Protoenstatite ($MgSiO_3$)	18.6
Calcium Iron Silicate ($CaFeSi_2O_6$)	8.7
Potassium Silicate ($K_2Si_4O_9$)	10.5

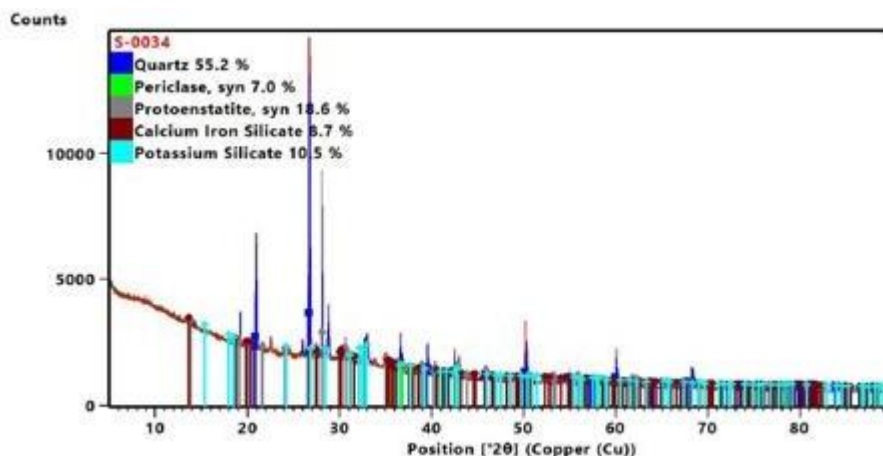


Figure 5: -Ray diffraction analysis of ceshew nut shell ash

Figure 5, shows the ceshew nut shell ash spectrum, it is possible to observe some peaks indicating the presence of crystalline material. These compounds are mainly composed by potassium (K), phosphorus (P), calcium (Ca), and silicon (Si) in oxid form. The peak intensity were high, reaching a maximum at 15000 counts, which means that the crystalline compounds were present in high amounts. The peak at $2\theta = 28^\circ$ appear to have a structure like graphite. The graphitization process can be classified into three regions based on the evolution of the peak intensity of the XRD pattern: the non-graphitization region, the near-graphitization region, and the graphitization region.

6. CONCLUSION

In the building sector, using plant biomass ash as a partial substitute for binder in cement-based structural mortars or grouts is an intriguing environmentally beneficial option. Additionally, recycling those ashes improves sustainability by lowering the amount of waste that accumulates in landfills and causes pollution. The physical and chemical properties of cashew nut shell ash (CNSA) are measured in the current study using X-Ray diffraction (XRD), Cashew Nut Shell Ash (CNSA) was shown the characteristics that are similar to those of cement by X-ray diffraction (XRD) and X-ray fluorescence (XRF). According to the study's findings, cashew nutshell is a cheap raw material that can be used to make activated carbon. The TGA profile indicates that the three main regions where weight loss occurs are drying, devolatilization, and residues (char and ash). The 1.35 weight percent is the outcome of an initial process that causes water molecules to be lost between $25^\circ C$ and $105^\circ C$. The moisture content decreased by 3.76% of the sample weight at temperatures below $110^\circ C$. There is a significant amount of magnesium oxide (25.85%), silicon dioxide (24.33%), potassium oxide (12.974%), calcium oxide (11.815%), and ferric oxide (8.071%) in cashewnut shell ash.

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