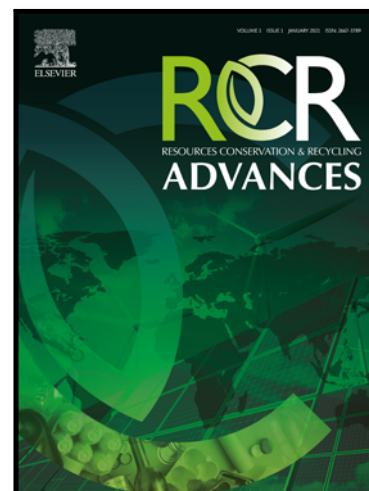


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Biochar in cementitious composites: A comprehensive review of properties, compatibility, and prospect of use in sustainable geopolymer concrete

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Highlights

- Biochar could be used as an alkaline activator in geopolymer concrete
- Pyrolysis pressure, temperature, heating rate, and resident time control biochar properties
- Unlike OPC concrete, geopolymer concrete can contain high volumes of biochar
- Fly ash could be replaced by biochar in order to meet alumina-silica demands
- Mixing biochar with water may produce an alkaline activator solution

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RESEARCH PAPER

Biochar in cementitious composites: A comprehensive review of properties, compatibility, and prospect of use in sustainable geopolymers concrete

(Title contains 18 words)

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Abstract

Geopolymer concrete (GPC) finds great potential in reducing global warming emissions from the construction sector. The conventional GPC precursor binders (fly ash, slag, metakaolin, silica fume, etc.) and alkaline activators are expensive, pollution-causing, and insufficient to meet the global requirement of concrete. Biochar (BC), agricultural waste produced through pyrolysis has rapidly been employed in cementitious composites since last decade because of its low cost, low carbon footprint, and ecological advantages. This paper presents a detailed review of the compatibility of BC with GPC, the properties (physical, chemical, and mechanical) in cementitious composites, and the chemical suitability of BC with GPC. The physical and chemical properties of BC can be controlled and highly depend on its production method (temperature, pressure, heating rate, resident time). The BC rich in silica and alumina is a feasible alternative to the solid precursor in geopolymer composites by controlling the particle size and mix design. The formation of a highly alkaline BC with water ensured its compatibility as an alkaline activator solution. They revealed comparable strength to GPC produced using conventional activators. Future studies are needed to investigate BC's experimental and practical applications as a precursor and alkaline activator in geopolymer composites.

Keywords: Biochar; Geopolymer concrete; Waste in construction; Alumina-silica source; Alkaline activator.

1. Introduction

The construction sector contributes significantly to environmental deterioration and worldwide carbon emissions (Guoru et al., 2023). As climate change substantially impacts

many businesses, there is a growing push for sustainable growth. An expanding requirement exists for eco-friendly construction materials and practices. Using BC for new and sustainable building and construction materials has appeared as one of the areas of research and development that is being encouraged. For ages, BC, a carbon-rich substance produced by pyrolysis (burning biomass without the presence of oxygen), used as soil modification to increase agricultural production efficiency (Agegnehu et al., 2017; Arif et al., 2020; Qian et al., 2015). However, its application in the building sector, notably in geopolymer concrete making, is relatively new, giving enormous capability for carbon sequestration and lowering greenhouse gas releases toward sustainable development (Mona et al., 2021; Tan, 2019). BC's porous nature and large surface area make it an ideal nominee for increasing concrete functioning (Chia et al., 2015; Leng et al., 2021).

Concrete, a blend of cement, aggregates, water, and admixtures, is the 2nd most widely used material on earth following water (Arif et al., 2021; Miller et al., 2018). Ordinary Portland cement (OPC) manufacturing requires high energy and consumes many raw materials. Along with this, a lot of waste (particularly CO₂) is discharged into the open environment, promoting global warming (Bellum et al., 2020a). The production of one ton of cement produces 0.98 tons of CO₂, which is near 6-7% of global CO₂ releases (Carbone et al., 2022). Many studies conducted in the past (for example, the use of fly ash (Oner et al., 2005), rice husk ash (Al-Khalaf and Yousif, 1984), slag (Shi et al., 2008), waste glass powder (Aliabdo et al., 2016), crumb rubber (Bisht and Ramana, 2017), waste brick powder (Arif et al., 2021; Khitab Anwarand Khan, 2022), glass and marble powder (Ahmed et al., 2020), etc., to find viable substitutes for reducing carbon footprints. The dilemma with all of them is that the replacement level works up to a certain limit. Moreover, many long-term durability issues (sulphate attack, acid attack, freeze and thaw, permeability, carbonation, sorption, etc.) are associated with these materials. BC has acquired significant concentration from researchers in the preceding decade, as its use in cementitious mixtures has comprehensively improved performance. Akhtar et al. (Akhtar and Sarmah, 2018), Sirico et al (Sirico et al., 2021), Restuccia et al. (Restuccia et al., 2020), and Aziz et al. (Aziz et al., 2023) concluded an optimistic influence of BC on the mechanical properties of concrete as the partial insertion caused a remarkable increase in mechanical properties and fracture toughness. Tan et al. (Tan et al., 2021), Mishra et al. (Mishra et al., 2023), Praneeth et al. (Praneeth et al., 2020), and Suarez-Riera et al. (Suarez-Riera et al., 2020) showcased BC's potential as a cement replacement in concrete that ultimately reduces carbon footprints. Zanotto et al. (Zanotto et

al., 2024) studied the decay character of reinforcing steel bars in concrete having BC dosage and exposure to CaCl_2 solution. They reported improved mechanical properties and comparable chloride diffusion tendency to OPC-based concrete under dry exposure. However, the BC dosage does not express its potential regarding the durability of concrete, as its addition promotes carbonation and reduces freeze and thaw resistance (Jia et al., 2023)(Jia et al., 2023). Jia et al. (Jia et al., 2023)(Jia et al., 2023) and Legan et al. (Legan et al., 2022) emphasized the necessity for more studies to entirely identify the continuing performing and ecological consequences of BC in traditional construction materials and geopolymer concrete composites.

Geopolymer concrete (GPC) has arisen as an ecologically welcoming substitute to OPC-based concrete; wherein OPC is replaced with waste material high in alumina-silica (Al-Si) content and polymerized in a basic medium to generate a three-dimensional tetrahedral polymeric structure with Si-O-Si and Si-O-Al bonds. The conventional GPC uses geopolymer binder (fly ash, slag, metakaolin, GGBFS, or other aluminosilicate source materials) instead of traditional cement binder. The problem associated with GPC is that the waste materials like fly ash (FA), metakaolin (MK), silica fume (SF), ground granulated ballast furnace slag (GGBS), etc. used as an Al-Si source are not abundantly available. Comparably, because of global sustainability protocols like the continuous closure of coal-fired power plants and the decline in the demand for thermal coal as an energy source, as well as ongoing energy reforms, renewable energy targets (RET), and state government privatization agendas for electricity in recent years, their production is also declining over time (Assi et al., 2020a). As per the report of the Ash Development Association of Australia, the yearly total generation of coal combustion products decreased by 0.6 million tonnes from the year 2020 to 2021. It is anticipated that the source of fly ash will become a challenge shortly because of the 10% decline in generation capacity projected to hit in the next 3 years (*CCP-A valuable Resource Ash Development Association of Australia Annual Production and Utilisation Survey Report*, n.d.). Moreover, the availability of FA, slag, MK, or SF does not meet the requirements to replace them 100% with cement (Assi et al., 2020a). There is a need for a more sustainable and alternative resource for depleting fly ash from coal combustion products. Hamed et al. (Hamed et al., 2024) used SF along with FA, Arslan et al. (Arslan et al., 2024) incorporated a mixture of GGBFS, SF, and MK, Wang et al. (Wang et al., 2024) added SF and calcium aluminate cement with FA, Bayrak et al. (Bayrak et al., 2024) reported the use of GGBS, SF, and RHA, and Huseien et al. (Huseien et al., 2018) utilized GGBS, waste ceramic, and waste

bottle glass with FA to produce high-strength, sustainable, and environment-friendly geopolymer composites.

BC is a renewable and ecologically friendly substance rich in Al and Si, performing remarkably well in cementitious composites to boost their mechanical and durability qualities might be used instead of conventional Al-Si sources and alkaline activators in GPC production by carefully monitoring mix design (Akhtar and Sarmah, 2018; Chia et al., 2015; Tayyab et al., 2023; Yang and Wang, 2021). Tan et al. (Tan et al., 2020) and Gupta et al. (Gupta et al., 2018b) explained BC added mortar mixtures showed a 10-30 % decrease in workability based on the type of BC and substitution level due to water absorption or porous structure of BC (Choi et al., 2012). Qing et al. (Qing et al., 2023) studied the properties of concrete having corn straw BC dosages (0-15% by weight of cement) and reported a 5.3% and 36.65% increase in compressive strength and fracture toughness at 1% and 3% (by wt. of cement) addition level respectively. Another study found that adding 3% (by weight of cement) of pyrolyzed BC at 500°C to cement after 28 days enhanced compressive strength by 19.8% due to its filling action and water-holding expertise (T. Chen et al., 2022). The denser and more compact matrix is produced using small-sized BC particles, facilitating efficient stress redistribution (Gupta et al., 2018b). The addition of 2% (by vol. of cement) BC decreased the autogenous dry shrinkage by 10% proving the resistance towards water evaporation (Du et al., 2023). The intrusion of 4% (by vol. of cement) BC in the concrete mix lowers permeability by 17.3% contrasted to OPC. Also, the strength loss by sulphate attack is 6.9% and 7.4% at 2% and 4% BC substitution (by volume of cement) respectively, compared to 8% for ordinarily water-cured concrete, making it more durable (Aneja et al., 2022). The replacement of OPC with 30% BC (by weight) as aggregate and 9% metakaolin (by wt.) as a binder could sequester 59 kg CO₂ per ton and potentially trigger an overall profit of 35.4 USD/ m³ (L. Chen et al., 2022c). Regarding the BC market trends, it has been evaluated at \$1.8 billion globally in 2022 and the cumulative yearly trend will expand from this base value to reach \$16 billion in 2028 over the years 2023-2028 as shown in Fig. 1 (Market, 2023). The key drivers of expansion include increasing knowledge of soil-borne illnesses, raising concern about worldwide food security, and requirement for high-quality, nutritionally dense food grains.

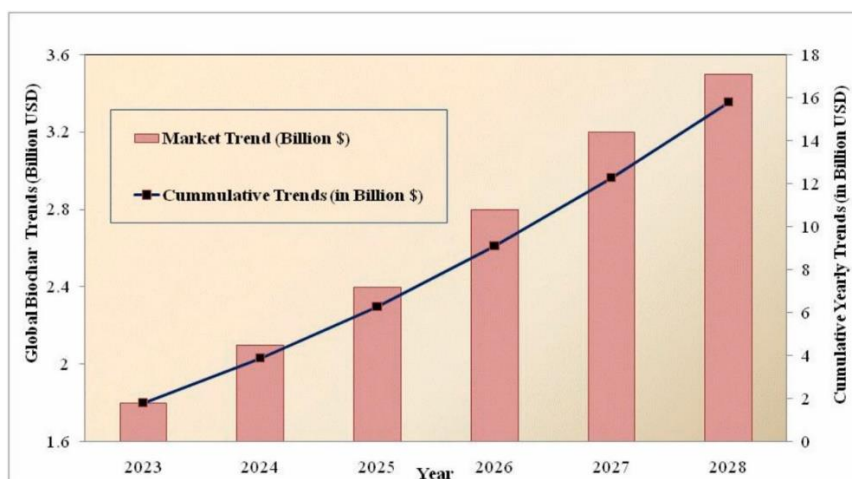


Fig. 1: Biochar market growth projection trends globally (Market, 2023).

Global reliance is increasingly transitioning towards fulfilling energy requirements through renewable energy sources (RESs). The exploration of agricultural waste biomass as a RES has been conducted in several countries, such as India, China, Denmark, Poland, and Nigeria (Potnuri et al., 2023). In countries such as Sweden, Denmark, and Poland, more than 50% of energy needs are fulfilled by RESs (Demirbas, 2008). In the United States, biomass accounts for around 5% of the nation's primary energy consumption (Haque Shama E. and Rafi, 2024). The Sustainable Development Goals set forth by the United Nations seek to significantly enhance the share of renewable energy within the global energy mix by the year 2030, and it is anticipated that renewable energy sources will meet 20%–40% of the global energy demand by the year 2050 (Nazir et al., 2020). This will enhance the generation of residual biomass ashes (Athira et al., 2021), which can be utilized in the creation of geopolymer composites. Each year, around 4 billion tons of cement is generated for OPC concrete (Lehne and Preston, 2018), replacing OPC with GPC involves the available generation of 1.2 billion tons of FA from coal-fired power plants (Yadav et al., 2022), in addition to approximately 1.3 billion tons of agricultural waste produced annually (Lee et al., 2022). This indicates that utilizing this significant agricultural waste biomass in geopolymer composites is feasible. The BC market is growing with a compound annual growth rate of 13.4%, and the Asia-Pacific region is recognized as the principal area of expansion (Market, 2023). The evolution and advancement of technologies for BC production are ongoing, which will undoubtedly guarantee product consistency (Barbhuiya et al., 2024), especially when considering large-scale applications. A dependable, large-scale manufacturing technology is needed for large-scale applications to meet the annual demand for thousands of tonnes of high-quality BC. (Salo et al., 2024) conducted a study to ascertain the views of Nordic nations

about the burgeoning BC industry, revealing that 49% of respondents expressed interest in constructing new BC production facilities. The standardizations and quality control measures for BC must be ensured throughout large batches since changes in carbon content, porosity, and mineral composition might impair GPC performance (Gupta and Kashani, 2021). The European Biochar Foundation (EBC) is creating BC-building standards for safety and efficacy (Schmidt et al., 2016).

This review study is driven because of the mounting interest in BC as an innovative and green resource for GPC production. Since the necessity for environment-friendly substitutes becomes progressively evident, investigating the properties, production methods, and sustainability aspects of BC-GPC composites is vital. This review aims to secure existing facts comprehensively; it covers the definition, production, and properties of BC including various factors affecting BC yield and its potential role in the progress of new types of cementitious amalgams. It also covers recognizing the chemistry of BC for its compatibility with different material constituents (as an Al-Si source or an alkaline activator) in GPC production. Future trends, research possibilities, and challenges in BC-GPC composites are also identified. This information from this critical review will raise awareness of the issue and encourage the development and use of BC as a new material resource for sustainable, economical geopolymer concrete production.

2. Production and properties of biochar

It is assessed that about 998 Mt of agricultural waste is formed yearly in the world, wherein 80% are organic wastes (Sinha Abhas Kumar and Rakesh, 2021). This significant volume necessitates systematic ways to value add and use this trash in the construction sector. This section reviews the production of BC and its properties to guide the suitability for the use of this material in GPC production.

2.1. Biochar production

BC is a carbon-abundant material made by the thermochemical conversion of biomass through the pyrolysis method. The organic feedstock is burned in a pyrolysis chamber at high temperatures without oxygen. The maximum amount of carbon retained within the burned material results in the formation of carbonaceous inert. The thermal breakdown of biomass yields a mixture of solid (BC), liquid (bio-oil), and gas (syngas) products. Different BC feedstocks are shown in Fig. 2. Table 1 provides a brief of the most prevalent ways for

producing BC, as well as the kind of biomass suited to each process and information on BC output.

Table 1: Summary of yield, relevant biomass, benefits, and challenges of different biochar production approaches.

Production method	Biochar yield (x of initial biomass) %	Applicable biomass	Advantages	Challenges	Reference
Traditional kilns	10-20	Wood, organic waste, crop residues.	Simple and low-cost method.	Inefficient yield and quality.	(Mekuria et al., 2012)
Gasification	15-30	Animal manure, woody biomass, crop residues.	Produce both biochar and syngas. Higher energy recovery.	Complex technology	(Ferreira et al., 2017; You et al., 2017)
Hydrothermal carbonisation	10-30	Wet organic materials, sewage sludge, organic waste	Low-temperature process.	Suitable for wet biomass. Longer processing times.	(Kumar et al., 2011; Regmi et al., 2012)
Pyrolysis	20-40	Wood, agricultural residues, organic waste	High quality and stability.	Energy-intensive process.	(Zahed et al., 2021)
Microwave pyrolysis	50	Agricultural residues, wood, lignocellulosic materials	Rapid process.	High initial investment.	(Arafat Hossain et al., 2017; Hadiya et al., 2022)

Pyrolysis converts dangerous wastes into valuable and sustainable products that benefit health and the environment. Through pyrolysis, the desired products can be produced by varying performance constraints like temperature, pressure, heating ramp, and duration. Pyrolysis may be slow (<100K/min at 300°C) or fast (>100K/min at 500°C or more) depending on temperature ramps and operating temperatures. Slow pyrolysis is effective in terms of product yield and quality. The emissions from the pyrolysis process can differ based

on the feedstock, temperature, and specific process situations (Conesa et al., 2020; Rahman et al., 2023a; Schwartz et al., 2020; Zaman et al., 2017). Some primary emissions are given in Fig. 3. Proper control and treatment of pyrolysis emissions are essential to minimize environmental impact and ensure the safety and efficiency of the process. This can involve gas cleaning systems, scrubbers, and filters to capture and neutralize harmful substances before they are released into the atmosphere (Pivato et al., 2024; Schwartz et al., 2020). The physical, chemical, microstructural properties and yield of BC highly depend on feedstock, particle size, pyrolysis temperature, pressure, residence time, heating rate, and method of pyrolysis given in Table 2 (Zahed et al., 2021). Fig. 4 shows the visual attributes of raw biomass feedstocks and subsequent BC in ungrounded and grounded states.

The process of converting biomass into BC through pyrolysis necessitates an energy input that fluctuates based on various factors, including the type of feedstock, the temperature of pyrolysis, and the rate of heating. The pyrolysis process generates BC, bio-oil, and syngas. The quantity of products varies based on the feedstock, and pyrolysis conditions. For example, (Hasan et al., 2021) concluded 43%, 27%, and 25% production of bio-oil, BC, and syngas respectively from pyrolysis of municipal solid waste. A study (Weldekidan et al., 2019) determined that the chicken litter and rice husk require 1.2 MJ/kg and 0.8 MJ/kg of energy for pyrolysis (500 °C, 10°C/min), respectively, with total recoverable energy values of 12.7 MJ/kg and 13.9 MJ/kg, corresponding to 84% and 89% efficiency, assuming heat is provided by combustion of the pyrolytic gas products. The efficiency of pyrolysis can be enhanced if the pyrolysis is driven by solar thermal energy along with bio-oil and syngas byproducts as energy sources (Weldekidan et al., 2019).

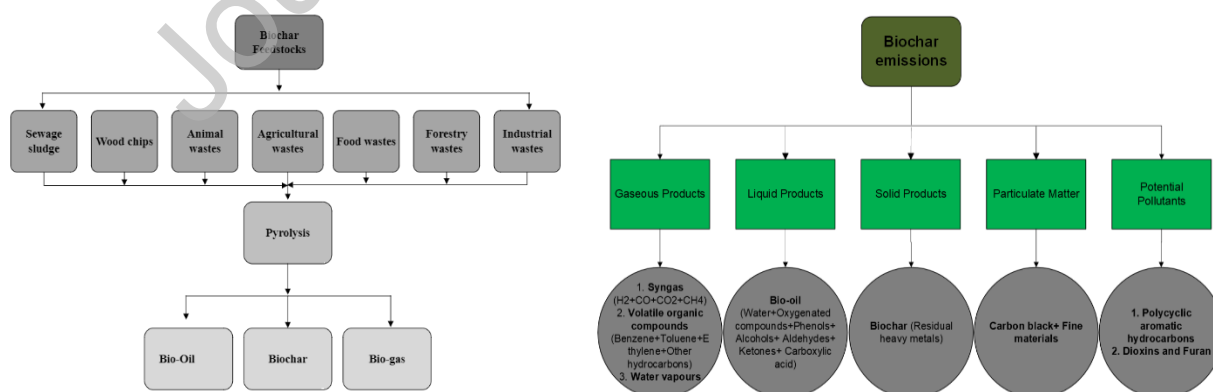


Fig. 2: Different feedstocks for biochar production (Srivatsav et al., 2020)

Fig. 3: Different emissions coming out because of pyrolysis (Conesa et al., 2020; Rahman et al., 2023a; Schwartz et al., 2020; Zaman et al., 2017)

Table 2: Summary of literature on using materials of different particle sizes, pyrolysis temperature, heating rate, pressure, and resident time for producing biochar.

Sr #	Material used	Property	Result	Reference
1	Coconut shells, Olive waste, straw, and hardwood	Particle size	The yield of biochar increased by increasing particle size.	(Sundaram and Natarajan, 2009; Zanzi et al., 2002)
2	Vine shoots	Particle size	Large feedstock particles led to stable product	(Manyà et al., 2014)
3	Municipal solid waste	Particle size	High syngas and low biochar yield were produced using smaller-sized particles.	(Luo et al., 2010)
4	Bamboo, Hickory wood, bagasse, and bamboo	Pyrolysis temperature	Yields of 80% and 30% at 300°C and 600°C respectively. The yield was maximum at low temperatures, while high temperatures resulted in a stable product.	(Hernandez-Mena et al., 2014; Sun et al., 2014)
5	Oil distillation residue, Soybean stover and peanut shell	Pyrolysis temperature	High carbon content, pore volume, enhanced aromaticity and surface area of biochar were achieved at high temperatures.	(Ahmad et al., 2012; Hao Li et al., 2017)
6	Wheat straw, Scrap tyres, Rice straw	Heating rate	An increase in the heating rate triggered biochar yield, surface area and size of holes.	(Fu et al., 2012; Mani et al., 2010; Williams et al., 1990)
7	Moso bamboo (Phyllostachys edulis)	Heating rate	Higher rates led to less liquid and solid contents and enhanced specific areas.	(D. Chen et al., 2014)
8	Pine, Coal, Rice husk and sawdust	Pyrolysis pressure	Physical and chemical properties were affected by pyrolysis pressure. The rate of reaction decreased and yield increased with an increase in pressure.	(Newalkar et al., 2014; Waghmare et al., 2016;

				Yun and Lee, 1999)
9	Pine sawdust	Pyrolysis pressure	High pressure endorsed extra yield by secondary oil cracking enhanced structure and compactness.	(Xu and Li, 2017)
10	Rapeseed stem	Resident time	The surface area and morphology were enhanced by increasing resident time.	(Zhao et al., 2018)
11	Peanut husk, rice husk, cornstalk, tobacco stalk, Palm kernel shell	Resident time	The pH and carbon content increased while the yield decreased with resident time and temperature rise.	(Cao et al., 2018; Mohd Hasan et al., 2018)

Many researchers studied different types of feedstocks and proposed optimal parameters for producing high-quality and high-quantity BC. They suggest that the slow pyrolysis method is the most efficient, considering the yield and quality of the product. Table 3 represents the optimal values of different variables involved in producing BC that best suits cementitious applications.

Table 3: Optimal values of parameters involved in biochar production from different feedstocks through slow pyrolysis (Heating rate = 1-10 C/sec., and pressure = 1 atm.). Pinewood (PW), Peanut shell (PS), Soybean stover (SS), Wheat straw (WS), Rice straw (RS), Paper mill sludge (PMS), Rice husk (RH), Wood bark (WB), Banana peduncle waste (BPW), Millet (ML), Maize (MZ) (Akhil et al., 2021; Akhtar and Sarmah, 2018; Amalina et al., 2022; Barbhuiya et al., 2024; Cao et al., 2018; Chia et al., 2015; Leng et al., 2021; Maljaee et al., 2021a; Shaaban et al., 2014; Tayyab et al., 2023)(Akhil et al., 2021; Akhtar and Sarmah, 2018; Amalina et al., 2022; Barbhuiya et al., 2024; Cao et al., 2018; Chia et al., 2015; Leng et al., 2021; Maljaee et al., 2021a; Shaaban et al., 2014; Tayyab et al., 2023).

Biochar type	Temperature (°C)	Residence time (min.)	pH	Surface area (m ² /g)	Volume (cm ³ /g)	Yield (%)
PW	500	30	8.7	380	0.15	30-35
PS	700	180	11.57	448.2	0.20	20-25
SS	700	180	11.32	420.3	0.19	18-22
WS	600	180	9.1	183.3	0.091	25-30

RS	600	180	9.7	156.2	0.084	25-30
PMS	600	120	9.17	50.44	0.074	35-40
RH	500	120	7.99	230.91	-	30-35
WB	500	30	9.8	350	0.14	30-35
BPW	462	80	11			35-40
ML	550	30	-	-	-	25-30
MZ	500	30	-	-	-	25-30

Overall, to achieve a high yield of BC, biomass should be pyrolyzed at high pyrolysis pressure, low temperature, increase in heating rate, at low resident time, and using a larger particle-size feedstock. The higher particle size led to a stable product. High carbon content, pore volume, surface area, and aromaticity of BC were attained at high temperatures, high heating rates, and resident times. The pH of BC increased by high heating residence time.



Figure 4: Grounded and ungrounded biochar produced from raw biowastes through pyrolysis.

2.2. Physical Properties

BC produced through pyrolysis is highly alkaline (pH is up to 12) in nature (Lehmann, 2007; Mukherjee et al., 2011; Mukherjee and Lal, 2014). This is because the acidic functional groups are eliminated, and salts of alkali and alkaline earth elements become augmented during carbonization (Fuertes et al., 2010), including readily soluble salts, carbonates, sparingly soluble metal oxides, hydroxides, and silicates that favour the geo-polymerization reaction in GPC (Singh and Singh, 2019). The pyrolysis temperature effect significantly the

pH of BC. The increase in temperature improves the alkalinity as reported by many researchers using various agricultural wastes in the past (Chaukura et al., 2017; D. Chen et al., 2014; Singh Yadav et al., 2023; Yuan et al., 2011; Zhang et al., 2015). The porous nature influences the alkaline-activator solution holding capacity of GPC which will result in improved geo-polymerization reaction's health and ultimately increased strength (Yuying Zhang et al., 2022a). Since BC has the promise for long-term carbon sequestration, this will promote stability and resistance to degradation of produced GPC using BC as a precursor (Li and Tasnady, 2023). Moreover, BC's high specific surface area will offer more reaction spots for geo-polymerization chain reaction (B. Zhang et al., 2022). All these qualities differ based on the manufacturing method, feedstock type, and pyrolysis circumstances, as indicated in Table 4.

Table 4: Physical properties of biochar using different biomasses at different pyrolysis conditions.

Property	Study	Result	Dependence	Reasons	Reference
pH	The alkalinity of biochar produced using different feedstocks and at different pyrolysis temperatures is found.	>7 Alkaline	1. Nature of biomass 2. Pyrolysis temperature \propto pH	Presence of metal oxides The functional groups (carbonyl, carboxyl, hydroxyl, etc.) detached and formed a basic medium.	(Chaukura et al., 2017; T. Chen et al., 2014; Hongbo Li et al., 2017; Singh Yadav et al., 2023; Yuan et al., 2011; Zhang et al., 2015)
Specific surface area	1. Pyrolysis of vine shoot and corn stover @ 350 and 500 °C 2. Pyrolysis of pine wood at 400–900 °C	1. SSA of VS & CS biochar ranged from 134 to 217 and 123–211 m ² /g, respectively 2. SSA of PW biochar increased from 28.7 to 347 m ² /g	Pyrolysis temperature \propto SSA	The breakdown of biochar resulted in the formation of meso- and micropores, which increased SSA.	(Balmuk et al., 2023; T. Chen et al., 2014; Keiluweit et al., 2010)

Bulk density	1. Wood chips biochar at different pyrolysis temperatures 2. Different carbon retaining biochar specimen's density	1. Bulk density decreased from 0.35 to 0.3 g/cm ³ by increasing temperature from 300 to 500°C. 2. A positive relationship b/w carbon content and bulk density of biochar	1. Pyrolysis temperature \propto 1/bulk density 2. Carbon content \propto 1/bulk density	1. More porosity is seen when subjected to high temperatures, causing density reduction. 2. The bulk density was reduced because of lightweight carbon concentration.	(Abdullah and Wu, 2009; Maljaee et al., 2021a)
Porosity	1. Pore's behaviour of differently sourced biochar at different temperatures 2. Microscopic study of the surface of biochar from rice waste, sawdust, and food waste	1. Highly porous material 2. Honeycomb-like pore structure. Biochar made at 500 °C confirmed more uniformly shaped, and closely spaced pores than produced at 300°C.	1. Pyrolysis temperature \propto porosity. 2. Pyrolysis temperature \propto formation of honey-comb particles	1. During pyrolysis, volatiles and organic materials are released, causing pores to develop in the biochar. 2. Biological capillary structure of biomass or release of volatile matter from source.	(Gupta et al., 2018a; Rehrach et al., 2016; Shaaban et al., 2014)
Solubility with water		Hydrophilic material		The formation of hydrogen bonds between hydroxyl groups on the surface of biochar and water molecules.	(Shafizadeh, 1982)

2.3. Chemical Properties

BC generally comprises carbon C, hydrogen H₂, nitrogen N₂ (above 95%), inorganic elements, and traces of heavy metals, including K, Ca, Mg, Na, P, S, Si, Al, Cl, etc., that are all varied in proportion based on the pyrolysis conditions and nature of feedstock. The high carbon content is due to the presence of hemicellulose and lignin, which generate stronger bonds in the GP matrix, maintain the alkaline environment, and function as a micro filler, contributing to matrix densification and reducing porosity (Wang et al., 2018). Fig. 5, Tables

5, and 6 show the intensity of SiO_2 , Al_2O_3 , and CaO from different agricultural and industrial wastes representing relatively higher contents of silica and alumina, which could be favourable to producing calcium aluminate silicate hydrate (C-A-S-H) gel during polymerization (Nguyen, 2021; Xiao et al., 2018). Nguyen (Nguyen, 2021) indicated the changes in pyrolysis temperature and biomass collection sources had a substantial impact on the chemical compositions, resulting in variable oxide concentrations. la Rosa et al. (de la Rosa et al., 2014) conducted an analysis characterizing the physical and chemical properties of four types of BC (wood, paper sludge, sewage sludge, and grapevine wood) samples through the field emission scanning electron microscopy (FESEM) images and Energy-dispersive X-ray spectroscopy (EDS) of the BC samples shown in Fig. 7. Fig. 6(A) shows the high calcium content of wood BC and mineral crystals deposited on the hollow region. Fig. 6(B) shows major carbon, oxygen, silicon, potassium, and calcium concentrations in paper sludge BC. The sewage-sludge BC shows a diverse chemical composition of aluminium, potassium, calcium, silicon, phosphorus, and iron on the surface shown in Fig. 6(C). Lastly, Fig. 6(D) demonstrates a rich content of carbon, potassium, and calcium, in grapevine wood BC (de la Rosa et al., 2014). Overall, the presence of an appreciable amount of SiO_2 , CaO , Al_2O_3 , Fe_2O_3 , etc., in agricultural and industrial waste produced BC that are the primary constituents for the hydration reaction (formation of calcium-silica-hydrate C-S-H gel in OPC and calcium-alumina-silica-hydrate C-A-S-H gel in GPC) should favour the polymerization reaction and will emerge as a good, sustainable, and abundantly available precursor strengthening the potential of substituting conventional FA, slag, GGBS, etc. for geopolymer composites. Moreover, the BC rich in potassium oxide (K_2O) will produce a strong alkaline solution with water and can act as an alkaline activator in GPC (Murtaza et al., 2024).

Table 5: Biomasses from different categories collected for chemical oxide compositions (Vassilev et al., 2010).

Category	Biomass source
Wood and woody biomass	Alder-fir sawdust, balsam bark, beech bark, birch bark, Christmas trees, elm bark, eucalyptus bark, fir mill, forest residue, hemlock bark, land clearing wood, maple bark, oak sawdust, oak wood, olive wood, pine bark, pine chips, pine pruning, pine sawdust, poplar, poplar bark, sawdust, spruce bark, spruce wood, tamarack bark, willow, wood, wood residue

Herbaceous and agricultural grasses	Arundo, bamboo whole, Bana, buffalo, kenaf, miscanthus, reed canary, sorghastrum, sweet sorghum, switchgrass
Herbaceous and agricultural straws	Alfalfa, barley, corn, mint, oat, rape, rice, straw, wheat
Herbaceous and agricultural residues	Almond hulls, almond shells, coconut shells, coffee husks, cotton husks, grape marc, groundnut shells, hazelnut shells, mustard husks, olive husks, olive pits, olive residue, palm fibres-husk, palm kernels, pepper plant, pepper residue, pistachio shells, plum pits, rice husks, soya husks, sugar cane bagasse, sunflower husks, walnut blows, walnut hulls, walnut shells
Contaminated biomass	Currency shredded, demolition wood, furniture waste, mixed wastepaper, greenhouse-plastic waste, sewage sludge, wood yard waste
Mixture of biomass	Wood-agricultural residue, wood-almond residue, wood-straw residue

Table 6: Range of major oxides present in biochar sourced from different biomass beneficial for geo-polymerization (Maljaee et al., 2021a; Vassilev et al., 2010).

Oxide composition (%)	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	MgO	Na ₂ O
Wood and woody biomass	1.86-68.18	0.12-15.12	5.79-83.46	2.19-31.99	1.1-14.57	0.22-29.82
Herbaceous and agricultural grasses	8.73-84.92	0.67-2.59	2.98-44.32	2.93-53.38	1.42-8.64	0.09-6.2
Herbaceous and agricultural straws	7.87-77.2	0.1-5.57	2.46-30.68	12.59-38.14	1.67-14.1	0.16-3.52
Herbaceous and agricultural residues	2.01-94.48	0.11-14.6	0.97-44.13	2.29-63.9	0.19-16.21	0.12-26.2
Contaminated biomass	3.39-60.1	3.08-53.53	7.63-26.81	0.16-9.7	1.57-6.45	0.54-4.06

Mixture of biomass	34.75-57.83	9.77-11.35	11.51-25.7	3.11-7.76	2.31-4.77	1.25-3.18
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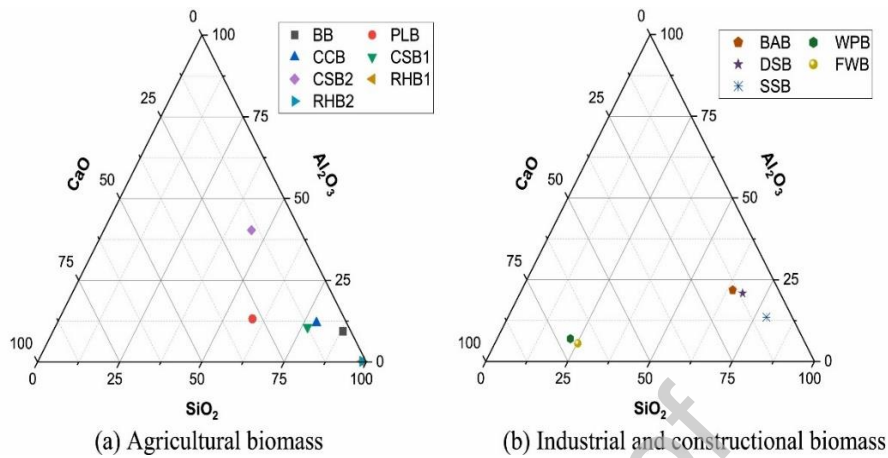
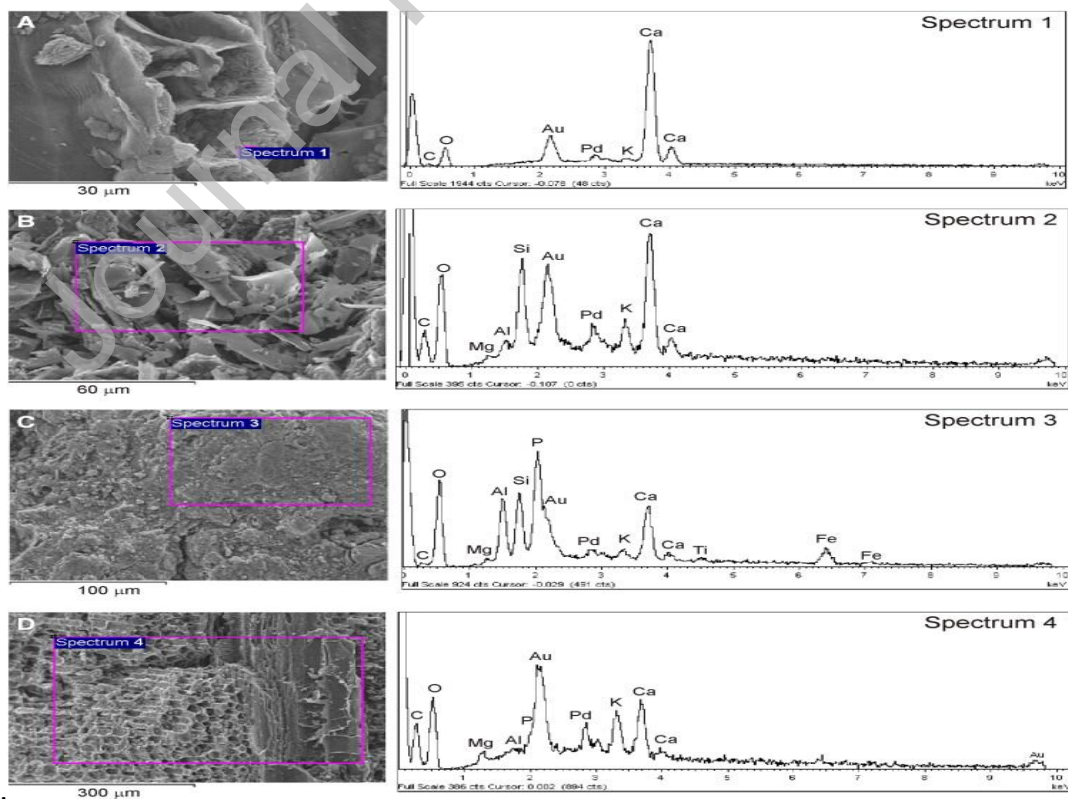


Fig. 5: SiO_2 , Al_2O_3 , and CaO concentration in BC produced from several agricultural and industrial wastes. Bagasse biochar (BB), Poultry litter biochar (PLB), Corn cob biochar (CCB), Corn stover biochar (CSB1), Corn straw biochar (CSB2), Rice husk biochar (RHB), Bamboo biochar (BAB), Waste plywoods biochar (WPB), Dewatered sludge biochar (DSB), Forest wood biochar (FWB), Sewage sludge biochar (SSB) (L. Chen et al., 2022a; Souradeep Gupta et al., 2021b; Khan et al., 2021; Maljaee et al., 2021b; Praneeth et al., 2022; Qin et al.,



2021).

Fig. 6: The biochar samples' EDS spectra and FESEM pictures (de la Rosa et al., 2014).

2.4. Biochar in cementitious composites

Recent studies indicate that cementitious composites can benefit from the addition of BC. The results from these studies on the characteristics of fresh and hardened concrete with varying percentages of BC are presented in the following sections.

2.4.1. Fresh properties

The exothermic reaction between cement and water, which releases a significant amount of energy, is the hydration of cement. The attendance of fine-size BC particles in the mix improved cement hydration because crushed BC leads to increased hydration products during the initial curing stage, because of the filler influences on the cementitious composites (Chi et al., 2022; Gupta et al., 2020a). Moreover, BC's larger surface area supplied further nucleation sites for the formation of binding products (Rodier et al., 2019). Dixit et al. (Dixit et al., 2019) observed an increase of about 5 wt.% BC dosage in concrete in place of cement could expedite the hydration process by up to 30%. Similarly, Gupta et al. (Gupta et al., 2020a) and Wang et al. (Wang et al., 2020) also concluded a rise of 10% and 7% in the hydration of cementitious composites by adding 5 vol.% of BC in place of cement respectively. Rodier et al. (Rodier et al., 2019) indicated that the degree of hydration of cementitious composites increased by about 9% at a 2 vol.% (of cement) dosage of BC.

BC is porous and absorbs water during the preliminary curing phase. This lessens the flowability and workability of the BC-cement blend as shown in Table 7 (Gupta et al., 2020b; J. Liu et al., 2022). As the proportion of BC in the mix rises, the mortar's workability tends to gradually decrease due to the porous nature and high carbon content of BC. It reveals high water demand, resulting in lowered workability. Throughout the mixes, the dosage of the superplasticizer can be adjusted to get the appropriate workability.

Table 7: Workability of concrete having a proportion of biochar sourced from different feedstocks.

Bio-feedstock	Pyrolysis temperature (°C)	Particle size (µm)	Replacement/addition by cement weight (%)	Flow reduction (%)	References
Wood chips	400	<500	0-5	10	(Sirico et al., 2022)

Saw dust	500	<200	0-5	13	(Gupta et al., 2018a)
Rice husk	450–550	<500	0-5	8	(Yang and Wang, 2021)
Waste wood	400-700	-	0-10	10-30	(Tan et al., 2020)

The use of BC may reduce the initial and final setting time of BC-cement mixes due to its tiny particle size and high heat of hydration (J. Liu et al., 2022; Yaashikaa et al., 2020) as given in Table 8. The time lessening was primarily due to BC's water absorption property as more alteration of cement greatly lowered the free water, resulting in a reduction in setting times (Haris Javed et al., 2022). BC powders enhanced the total formation of C-S-H gel during the initial hydration, minimizing the discrimination of the BC-cement mixture and resulting in quicker setting times (Gupta et al., 2018b). Depending on the temperature during the production process, BC can be either hydrophilic or hydrophobic and can join in micro-filling activity, both of which help to shorten the setting duration (Akinyemi and Adesina, 2020; Tan et al., 2020).

The hydrophilic character of BC functions as a moisture reservoir, gradually releasing water to sustain the internal curing of the cementitious matrix (Shafie et al., 2012), decreasing the water-to-cement ratio. However, an excessively low water-to-cement ratio may reduce the overall workability of the mixture as there is less free water to lubricate particles during mixing and placement, necessitating the incorporation of supplementary water-retaining admixtures. The biocidal effects of BC can inhibit microbial growth within the concrete, which is generally advantageous for durability. In some curing conditions, microbial interactions can break down organic contaminants or support hydration reactions (Kochanek et al., 2022). This impact must be comprehended to guarantee that the biocidal characteristics do not disrupt the setting or microstructural evolution of the geopolymer composites. The optimum biochar dose and particle sizes are essential to maintain hydration and geopolymerization of concrete and geopolymer composites respectively (Senadheera et al., 2023). Furthermore, sustaining optimal curing conditions, including regulated humidity, will facilitate hydration and polymerization while using BC's internal curing activity and biocidal attributes (Gupta et al., 2018a).

Table 8: Initial and final setting time of concrete having a proportion of biochar sourced from different feedstocks.

Bio-feedstock	Pyrolysis temperature (°C)	Particle size (µm)	Replacement/addition by cement weight (%)	Initial setting time reduction (%)	Final setting time reduction (%)	References
Coconut husk	500	<75	2	26	14.2	(Haris Javed et al., 2022)
Waste wood	300-500	<200	1	10.4	14.6	(Tan et al., 2020)
Peanut husk	500	<100	3	11.2	16	(Gupta and Kashani, 2021)

2.4.2. Hardened properties

The comparison of the hardened mechanical properties of concrete with BC are depicted in Fig. 7. Numerous studies have been carried out to assess BC's impact on concrete's compressive strength. The limited BC dosage significantly boosts compressive strength because of the substantial ability of water retention, which aids in internal curing. The flaky and angular surfaces of BC then provide strong bonding with the cementitious matrix. For example, Javed et al. (Haris Javed et al., 2022) examined how BC derived from bagasse feedstock affected the strength of concrete. An increase of up to 28% in strength compared to ordinary concrete at 2% (by vol. of cement) in addition to BC was found. Rashid et al. (Rashid et al., 2024), Choi et al. (Choi et al., 2012), and Akhtar et al. (Akhtar and Sarmah, 2018) found an increase of 23%, 15%, and 12% in strength at 5% (by vol. of cement) Jungli keekar, hardwood, and rice husk BC substitution levels respectively. Tayyab et al. (Tayyab et al., 2023) achieved an increase of 32% and 28% in mortar's compressive strength with the addition of 0.2% and 0.5% (by wt. of cement) millet and maize BC, respectively (Tayyab et al., 2023). The heat treatment to remove organic elements from untreated sewage increased the efficacy of BC. Fig. 7(a) shows that up to 10% replacement of cement with BC gives an increase or comparable strength to ordinary concrete specimens, and it decreases afterwards. This decline may be due to porous structure and the incongruence of the hydration process

outcome between cement and BC, as the magnitudes of CaO and SiO₂ in BC are less than in cement. As a result, fewer C-S-H products are formed and ultimately strength is reduced.

The tensile strength of cementitious composites either enhanced or kept around that of the control specimen by adding up to 3-4% of BC (by wt. of cement) is shown in Fig. 7(b). The angular, flaky, needle-like particle behaviour of BC strengthens the specimen's resistance to tension by acting as a reinforcing bridge between the cement matrixes. Li et al. (Li et al., 2023), Qin et al. (Qin et al., 2021) and Asadi et al. (Asadi Zeidabadi et al., 2018) concluded an increase of 30%, 16%, and 5% at 3% (by volume of cement) dosage of *Carya cathayensis* plant, waste plywood, and rice husk BC in cementitious composites, respectively. Ahead of the ideal dosage, the decrease in tensile strength was due to the agglomerate formation of BC, which promotes concrete's brittle behaviour.

BC up to 5% by volume enhances the flexural strength of cementitious material, as shown in Fig. 7(c). Khalid et al. (Khalid et al., 2019) achieved the maximum enhancement of 47% and 59% in flexural strength with the injunction of 1% of wheat straw and 1% cotton straw by volume of cement, respectively. This enhancement is due to the small particle dimension, and angular, needle-like shape of BC that provides a high contact area and bridging for bond generation in the host cementitious matrix. Using BC improved the internal curing of concrete by allowing the water to be gradually released during the curing process as the BC grew older that ultimately raised concrete's strength. However, as the amount of BC increased, tiny weak zones developed in the BC-adapted concrete because of the agglomeration effect, which quickly reduced the concrete's compressive strength (Gupta et al., 2018a).

Tayyab et al. (Tayyab et al., 2023) noted an increase of about 170% in fracture toughness at 0.5% (by wt. of cement) dosages of maize BC. The addition of carbonaceous nanoparticles significantly improves the fracture response of cementitious composites, as shown in Fig. 7(d). Fig. 11 depicts SEM micrographs of cement mortar samples that revealed the crack branching, deflection, and contouring mechanism. These processes change surface rupture into volumetric break, which increases the energy needed to shatter the sample (Khalid et al., 2019). The reduced quantities of finer BC, which possesses a finer texture compared to cement, might potentially facilitate a filling phenomenon, therefore compressing the cement matrix and enhancing the strength of concrete.

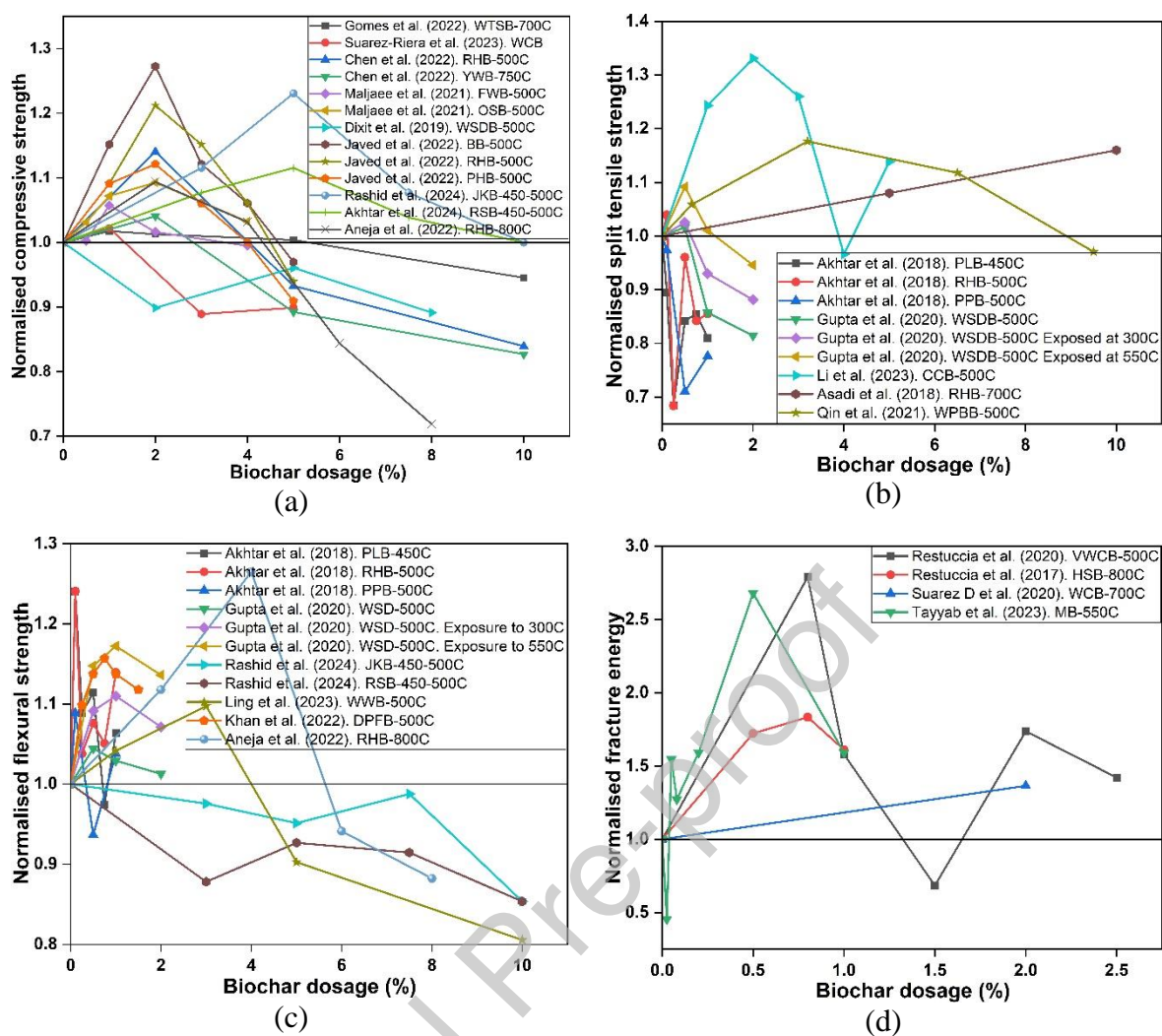


Fig. 7: Mechanical properties of cementitious composites as a function of biochar dosage. **(a)** Compressive strength **(b)** Split tensile strength **(c)** Flexural strength **(d)** Fracture energy. Water treatment sludge biochar (WTSB), Wood chips biochar (WCB), Rice husk biochar (RHB), Yard waste biochar (YWB), Forest wood biochar (FWB), Olive stone biochar (OSB), Wood sawdust biochar (WSDB), Bagasse biochar (BB), Peanut husk biochar (PHB), Jungli keekar biochar (JKB), Rice stubble biochar (RSB), Poultry litter biochar (PLB), Pulp and papermill biochar (PPB), *Carya cathayensis* biochar (CCB), Waste plywood boards biochar (WPBB), Date palm fronds biochar (DPFB), Virgin woodchips biochar (VWCB), Hazelnut shells biochar (HSB), Wood waste biochar (WWB), Maize biochar (MB) (Asadi Zeidabadi et al., 2018; L. Chen et al., 2022b; De Carvalho Gomes et al., 2022; Dixit et al., 2019; Haris Javed et al., 2022; Khan et al., 2022; Li et al., 2023; Ling et al., 2023; Maljaee et al., 2021b; Qin et al., 2021; Qing et al., 2023; Restuccia et al., 2017; Sirico et al., 2022; Suarez-Riera et al., 2023, 2020; Tayyab et al., 2023).

2.5. Microstructural properties

The spherical, tubular, ridge-like, and cellular-like particle nature of BC is confirmed in Fig. 8. Akhtar et al. (Akhtar and Sarmah, 2018) suggested that rice husk BC improves the performance of cementitious composites through the crack-branching and contouring phenomenon of crack resistance, as shown in Fig. 9 and Fig. 10. When the quantity of BC increased, more empty pores appeared in the concrete, boosting water absorption. This process results in a less compact structure, which leads to poor strength. This is because of the filling in the spaces in concrete, tricalcium silicate is depicted as a granular structure that transforms into Ca(OH)_2 and promotes weaker zones.

BC particles, characterized by their elevated specific surface area and porous architecture, function as micro-fillers in the cement matrix. When ingested at optimal dosages, can effectively occupy micro-voids, and diminish the interconnectivity of pores within the matrix. Research conducted by (Gupta and Kua, 2018) and (Yang and Wang, 2021) demonstrated that BC particles occupy voids and decrease pore size distribution, subsequently leading to a reduction in overall porosity and an enhancement in impermeability. Micro-fillers' impact is especially significant when utilizing smaller particle sizes, as these particles facilitate a more uniform distribution and enhanced packing within the cement matrix. The hydrophilic property of BC helps it to absorb and hold water during mixing and curing (Fan et al., 2022). Biochar slowly releases water while the cement or geopolymer matrix cures, enabling continual hydration and geo-polymerization. This internal curing action minimizes autogenous shrinkage and microcrack development, creating a denser microstructure (Mo et al., 2019). (Dixit et al., 2019) proved denser and more compact concrete matrix with reduced porosity and permeability utilizing BC.

The surface chemistry of BC often includes functional groups such as carboxyl, hydroxyl, and carbonyl groups, which can interact with the calcium and silicate phases in the cement matrix (Bao et al., 2022). This interaction enhances the bonding between BC particles and the surrounding matrix, reducing the formation of interfacial transition zones (ITZs), which are typically areas of higher porosity and weakness (Zhu et al., 2023). (Akhtar and Sarmah, 2018) indicated these chemical interactions promote a more homogenous microstructure with fewer weak zones reducing permeability. The incorporation of BC affects the pore structure by obstructing capillary pores and establishing a more convoluted route for fluid entry, hence diminishing permeability.

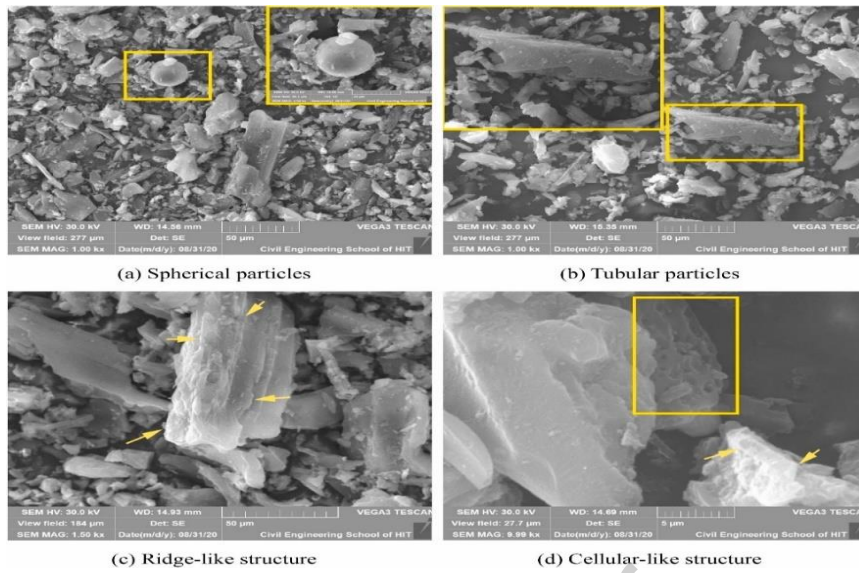


Fig. 8: SEM images of biochar particles (T. Chen et al., 2022).

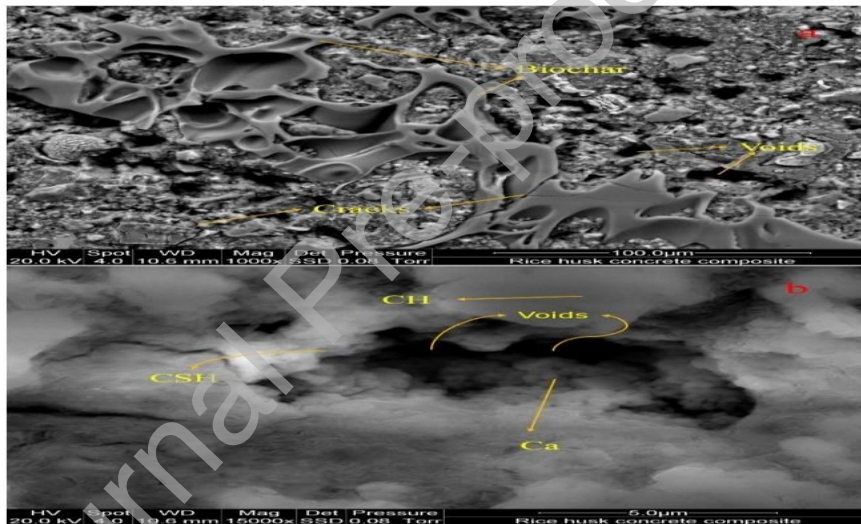


Fig. 9: SEM images of concrete (a) Rice husk biochar addition (b) Microstructure of biochar added specimen at higher magnification (Akhtar and Sarmah, 2018).

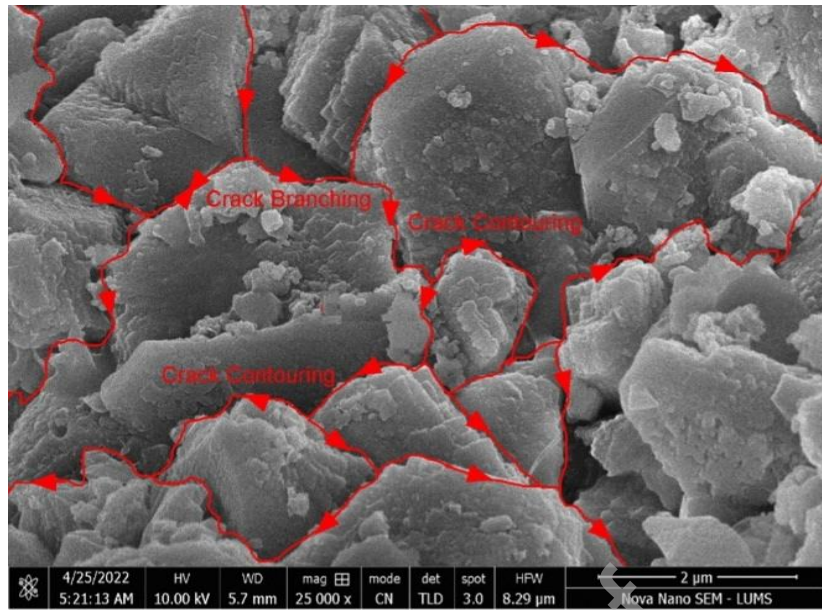


Fig. 10: SEM image of mortar: Crack deflections and contouring (Khalid et al., 2019; Tayyab et al., 2023).

To conclude this section 2, it is believed that the amalgamation of BC into cementitious composites offers a multifaceted approach to creating more sustainable, durable, and environmentally friendly construction materials that will not only improve the composite's strength but also get rid of the environmental burden of agricultural waste. There are challenges to be addressed, particularly regarding the dosage of BC as only a small concentration (up to 5% by weight or volume) is acceptable in place of cement in the cementitious matrix, also consistency and mix design remain questionable. The use of BC in geopolymer concrete hasn't been addressed in past studies. Since the binding product is different (C-A-S-H instead of C-S-H) in the GPC, there is a strong possibility of making BC a valuable addition in the GPC production as an Al-Si source or an alkaline activator, done through detailed microstructural, physical, chemical, mechanical, and durability analysis of GPC discussed in next section.

3. Geopolymer concrete: An overview

3.1. Composition and properties of geopolymer concrete

Geopolymer concrete (GPC) is an innovative construction material known for its sustainability and high performance. It is a substitute to conventional OPC concrete and is composed primarily of aluminosilicate materials. GPC is classified as the third-generation binder, following lime and OPC. GPC has developed as an ecologically friendly substitute for OPC-based concrete. OPC accountable for high CO₂ releases (Zhao et al., 2023) is entirely

replaced with alumina-silica (Al-Si) rich waste and undergoes polymerization reaction in a basic medium to generate a tetrahedral polymeric structure of Si–O–Si and Si–O–Al bonds (Ahmad et al., 2021). In 1979, Davidovits coined the term "geopolymer" to include a group of mineral binders, such as zeolites, that possess an amorphous microstructure and chemical composition (Chowdhury et al., 2021). It was formerly employed throughout the Roman Empire (Davidovits, 2015). The conventional GPC is a type of concrete that uses geopolymer binder (fly ash, slag, metakaolin, ground granulated blast furnace slag, or other aluminosilicate source materials) instead of traditional cement binder. An alkali activator solution (using alkali metal hydroxide and their respective silicates) is prepared that provides the basic environment necessary for polymerization reaction (Zhang et al., 2020). A three-dimensional Ca-Al-Si-H gel forms when an alkaline activator solution encounters an aluminosilicate source material, just like Ca-Si-H gel during hydration in OPC (Roy et al., 2022). Fig. 11 shows the essential constituent required for GPC production. Fig. 12 shows a typical contrast between OPC concrete and GPC, representing that GPC is superior, particularly concerning sustainability and durability properties.

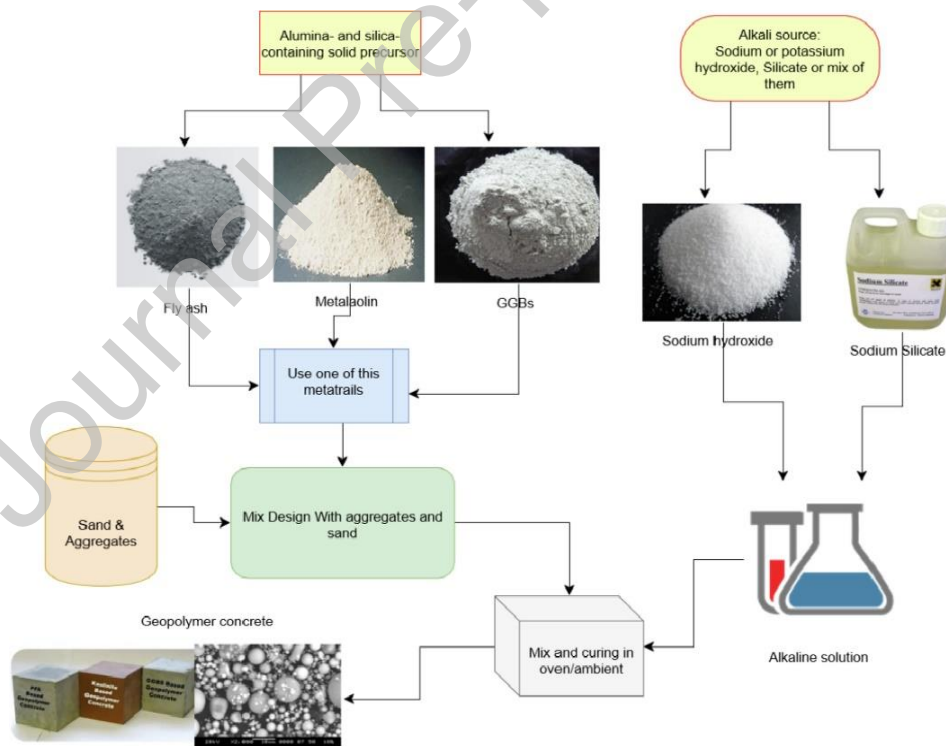


Fig. 11: A schematic diagram of constituents required for GPC production (Hassan et al., 2019)

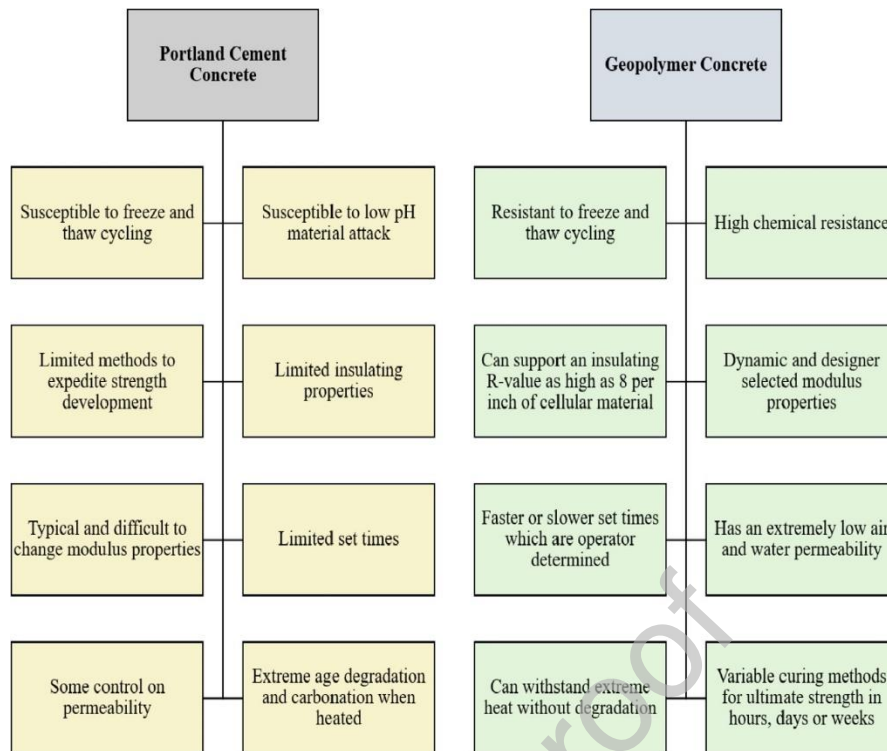


Fig. 12: Comparison of performance of OPC concrete and GPC (Hassan et al., 2019).

Many studies have reported exceptional mechanical and thermal properties, higher resistance to harsh environments, electromagnetic interference shielding, and durability of GPC as compared to OPC (Almutairi et al., 2021; Amran et al., 2020; Chen et al., 2023; Z. Liu et al., 2022; Novais et al., 2019; Singh et al., 2015). GPC is also excellent for backfill grouting material in shield tunnelling (Jiang et al., 2023). The Global Change Institute (Fig. 13) at the University of Queensland is the world's first structure to employ GPC efficiently (Bligh and Glasby, n.d.). The largest application in the world, the Brisbane Wellcamp Airport, saved 6600 tonnes of carbon emissions thanks to its construction, which used over 40,000 m³ of GPC as shown in Fig. 14 (Supriya et al., 2023). GPC also finds its positive applications in the construction of retaining walls (Ng Tian Singand Voo, 2012), marine structures like water tanks (Rahman and Al-Ameri, 2022), and precast bridge decks (Ahmad et al., 2019).



Fig. 13: Global Change Institute, UQ Australia: World's first public construction with structural GPC (Bligh and Glasby, n.d.).



Fig. 14: Brisbane West Wellcamp Airport Australia: World's greenest airport (Supriya et al., 2023).

3.2. Challenges in conventional geopolymer concrete

GPC is mainly produced using Al-Si source materials (e.g., FA, slag, MK, etc.) and alkali activation source materials (e.g., NaOH/KOH + Na₂SiO₃/ K₂SiO₃). The available quantity of these source materials is insufficient to replace 100% of OPC with GPC in the construction sector. Table 9 confirms the annual production of these materials and the requirements to eliminate OPC. FA is the main and most important source of Al-Si in GPC; its yearly worldwide production is 2.8 billion tons, whereas 100% OPC replacement requires 1.9 billion tons (Assi et al., 2020a). Fig. 15 illustrates that the globe is experiencing a shortage, except for China and India, the only two generating vast quantities and exhibiting excess. The availability of natural gas, the closing of coal-fired power plants, continuing energy reforms,

the goal of using renewable energy, and the state government's plan to privatize electricity are the causes of the shortfall. Australia consumes 85% of its generated FA in different sectors. Also, a reduction of 0.5 million tons over the reporting period and an additional 10% drop in generation volume will happen in the next three years (Ash Development Association of Australia, annual report, Jan-Dec. 2021) (*CCP-A valuable Resource Ash Development Association of Australia Annual Production and Utilisation Survey Report*, n.d.). Less than 1% of concrete production for a few years could be replaced with slag and metakaolin if all their reserves were extracted for use in GPC. The use of slag compromises the elastic and fracture energy properties of concrete. Sodium silicate (provides active silica for polycondensation of Al-Si, forming final tetrahedral structure) is the primary agent to activate alkali along with sodium hydroxide (high value of pH helps in dissolution of Si and Al in the precursor), sufficient to replace only less than 1% of ordinary concrete with GPC. Commercial methods to produce sodium silicate (SS) use either melting or hydrothermal methods. These techniques are environmentally burdensome because of the high temperature and pressure, generating roughly 1.514 kg of CO₂/kg of SS. Also, significant air pollution, such as nitrogen and sulphur oxides, adds to the environment. Apart from these impacts, these processes are costly owing to the fuel requirements needed to meet energy demands. China is the top Na₂SiO₃ producer, with 42% of global production, followed by Western Europe and the United States, with 1.9 and 1.42 million tons/year (Assi et al., 2020b). Some investigations revealed that GPC had more ozone depletion, acidification, and photochemical oxidant generation than OPC, which was related to CFC emissions during commercial activator manufacturing (Dal Pozzo et al., 2019; Salas et al., 2018)

Table 9: Annual production and requirement of Al-Si and alkali activation source materials for GPC.

Sr#	Materials	Nature of material's usage in GPC	Annual production (Mt)	Annual		Reference
				requirement to replace 100% OPC (Mt)	Surplus (+)/Deficit (-) (Mt)	
1	Fly ash	Al-Si source	2800	1900	+900	(Assi et al., 2020a)
2	Slag	Al-Si source	288	1700	-1412	
3	Metakaolin	Al-Si source	37	3700	-3663	
4	NaOH	Alkali activator	72	120	-48	
5	Na ₂ SiO ₃	Alkali activator	12	9.6	+2.4	
6	Silica fume	Alkali activator	1.9	-	+	

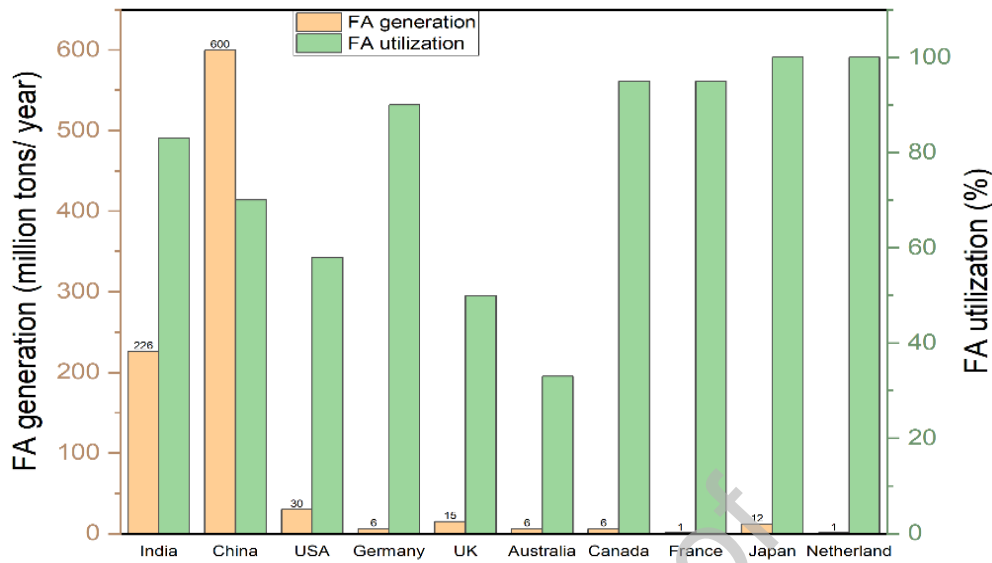


Fig. 15: Worldwide fly ash generation (million tons) and utilization (%) (Kumar and Paul, 2024; Luo et al., 2021; Nayak et al., 2022; Orozco et al., 2024; Sharma and Yadav, 2021; Shukla et al., 2023).

3.3. Sustainable alternatives in geopolymer concrete

The increased awareness of environmental and social issues such as resource conservation, waste reduction, energy efficiency, regulatory requirements, and market demand has made the need for sustainable alternatives in the manufacture of GPC more demanding. Current research is focused on manufacturing GPC from various industrial and agricultural wastes. Some critical studies on the consumption of waste materials in the manufacturing GPC are given in Table 10.

Table 10: The major findings of prior studies dealt with the manufacture of geopolymer concrete from different wastes.

Sr #	Material used	Alkaline solution	Major conclusions	References
1	Corn cob ash, GGBS	NaOH 12,14 &16 M	<ul style="list-style-type: none"> ✓ Specific heat capacity increased. ✓ Thermal conductivity and diffusivity reduced. 	(Oyebisi et al., 2022)
2	Fly ash, MK, GGBS	NaOH 14 M	<ul style="list-style-type: none"> ✓ Compressive strength is like or more than ordinary concrete. ✓ Drying shrinkage is lower than the control sample. 	(Amin et al., 2022)
3	Fly ash,	NaOH 8,12,16 M,	<ul style="list-style-type: none"> ✓ Compressive, flexural, and split 	(Parveen et

	alccofine	Na ₂ SiO ₃ / NaOH ratio 2.5.	tensile strength were maximum at 16 M NaOH concentration at ambient curing. ✓ Increasing molar ratio enhanced mechanical strength but reduced fresh characteristics.	al., 2018)
5	GGBS, SCBA	NaOH 12 M Na ₂ SiO ₃ / NaOH ratio 2.0	✓ 10% replacement is optimum to increase mechanical strength. ✓ Density increased up to the replacement of 20%. ✓ At a higher percentage of SCBA, the pH value was high.	(Kathirvel et al., 2020)
6	Fly ash, SCBA, and metakaolin	NaOH 12 M, Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 1:2.5	✓ For optimal mechanical strength and durability, use 10% SCBA and 20% metakaolin in place of FA.	(Singh, 2021)
7	Bottom bagasse ash, clay ash	NaOH (2,4,6,8,10,12,14,16 M) & Na ₂ SiO ₃	✓ Up to 8 M NaOH, Compressive strength increases and decreases with higher molarity. ✓ Maximum compressive strength is achieved when the activated clay content in bagasse ash clay mix is 60%.	(Amin et al., 2021)
8	Rice husk ash, GGBS	RHA: NaOH 1:0.5,1:1.0,1:1.5	✓ Good compressive strength for RHA synthesized activator at 2hr process.	(Rajan and Kathirvel, 2021)
9	Fly ash, red mud	NaOH 8 M& Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 2.5:1 & 2:1	✓ Better performance at a silicate-to-hydroxide ratio of 2.5.	(Bellum et al., 2021)
10	Fly ash, bamboo ash	NaOH 10 M& Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 2.55	✓ Better compressive strength performance with 95% FA + 5% BA at the early age of curing. ✓ At 800°C, utilization of BA exhibited the highest residual compressive strength.	(Ishak et al., 2019)
11	Coal fly ash, wheat straw ash, metakaolin	NaOH 6 M & Na ₂ SiO ₃	✓ 58% & 26% increase in compressive and flexural strength of GPC having non-wood biomass ash and	(Rakhimova and Rakhimov, 2019)

			specimens were cured in boiling water.	
			✓ An increase in fire resistance is also seen.	
12	Rice husk ash, ultrafine slag, corncob ash	NaOH 8 M & Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 2.5	<ul style="list-style-type: none"> ✓ The optimum dosage of corn cob in RHA-GPC is up to 6%. ✓ Improved durability and reduction in mechanical strength are seen in corncob ash and ultrafine slag. 	(Saloni et al., 2021)
13	Slag, silica fume	NaOH 14 M & Na ₂ SiO ₃	✓ Increase in mechanical properties.	(Jena and Panigrahi, 2022)
14	Cement, GGBFS	NaOH 10 M, the ratio of SiO ₂ to Na ₂ O 1.25 & water to binder is 0.4	<ul style="list-style-type: none"> ✓ When the curing time reached 90 days, the strength of alkali-activated slag concrete improved. ✓ Mixing copper slag with alkali-activated slag concrete results in reduced porosity, water absorption, and chloride penetration. ✓ Modulus of elasticity increased by increasing copper slag content. 	(Mithun and Narasimhan, 2016)
15	Fly ash (Class F), GGBFS	NaOH 14 M, Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 1.5,2.0&2.5	<ul style="list-style-type: none"> ✓ Up to 30% substitution of GGBS caused high compressive strength. The increase in basic solution concentration led reduction in compressive strength. ✓ Fly ash-based GPC for curing in ambient conditions can be balanced for appropriate flowability and setting time. 	(Nath and Sarker, 2014)
16	Fly ash, GGBS, cement	NaOH 8 M, Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 1:2.5	<ul style="list-style-type: none"> ✓ Higher compressive strength at ambient curing. ✓ Reduction of 4 to 15% in strength for oven-cured specimens compared to ambient- 	(Bellum et al., 2020b)

			cured ones.		
17	Cement, sugar can bagasse ash	NaOH 4,8,12 M & KOH	✓	Greater molar ratios reduced the mechanical strength. 8 M alkali activation solution gave optimum mix. GPC containing SCBA had a better fresh property.	(Rehman et al., 2020)
18	Metakaolin, sugar can bagasse ash	NaOH 6 M, Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 2,2.5,3.	✓	With the increase in Si/Al ratio up to 2.5 and 0.5 aggregate to binder ratio, the mechanical strength parameter improved. After 3 days of curing, GP mortars gain up to 60% strength.	(Yadav et al., 2020)
19	Ground granulated ballast slag, nano silica, Nano metakaolin	NaOH 12 M & Na ₂ SiO ₃ , Na ₂ SiO ₃ /NaOH ratio 2.33	✓	A meaningful development in hardened strength properties using ultimate 1% steel fibres, 4% nano-silica, and 6% nano metakaolin.	(Rabiah et al., 2020)

In summary, various alternative materials can be effectively used as binder materials in GPC manufacturing. Applying FA, GGBS, MK, rice husk ash, sugarcane bagasse ash, and red mud as Al-Si source material could improve the mechanical strength and durability of GPC. The physical, chemical, fresh, mechanical, and durability properties of GPC depend on various factors like the Si/Al ratio of precursor materials, Na₂SiO₃/NaOH ratio and dosage of alkaline solutions, curing period and conditions, etc. It is necessary for the waste that it should be chemically (amount of silica, alumina, lime, etc.) and physically (pH, surface area, particle size and shape, specific gravity, etc.) compatible with conventional GPC. The right dosage of constituents and the use of suitable methods and conditions promise good mechanical strength and durability of GPC. This would result in sustainable concrete development, increasing the greener environmental impact and minimizing the negative effects of greenhouse gas emissions.

4. Compatibility of biochar with geopolymer concrete

4.1. Activation of carbon present in biochar

BC is abundant in carbon (approximately 60-90%) and it is crucial to activate it before using it in GPC. AC is often produced to achieve a well-organized structure, a large specific surface

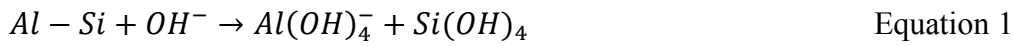
area, physiochemical stability, optimal pore size distributions, surface reactivity, and high adsorptive capacity. (Danish and Ahmad, 2018). AC's surface area can approach or surpass 1500 m²/g, more than fifty times that of ordinary BC (Azargohar and Dalai, 2006). To produce activated carbon, waste organic biomasses (agricultural wastes) are gradually replacing the non-renewable fossil fuel-based precursors (coke or coal) due to their economic viability, sustainability, lower production and renewal cost, and high carbon proportion (Mukherjee et al., 2019; Rashidi and Yusup, 2017). It can be made active using a physical or chemical approach. Physical activation involves heating BC to a high temperature (700-900°C) in the presence of an oxidizing agent such as steam, air, N₂, or CO₂ to enhance its surface area and porosity (Yahya et al., 2015). The complex and varied changes that occur during pyrolysis help the activation process (Wang et al., 2019). During chemical activation (economically and practically feasible), chemical agents with high dehydration potential (such as acids, alkalis, transition metal salts, etc.) saturate the precursor under an inert environment (450-900°C) (Nanda et al., 2016). Tehrani et al. (Tehrani et al., 2015) proved that chemically AC has the maximum surface area (696 m²/g) compared to AC obtained from physical activation (641 m²/g). Kumar and Jena (Kumar and Jena, 2015) reported significant yields (38.1 wt.%) of AC, together with a higher surface area (2869 m²/g) and total pore volume (1.96 cm³/g), achieved by chemical activation of Fox nutshell with the assistance of ZnCl₂. Shahkarami et al. (Shahkarami et al., 2015) concluded whitewood BC served as a precursor for physical and chemical activation processes. Using KOH as an activator produced a surface area of 1400 m²/g which is less compared to the BC. Since BC is produced at high temperatures in an inert environment, the alkaline activating agents (NaOH/KOH+Na₂SiO₃/K₂SiO₃) used in conventional GPC would surely activate the carbon present abundantly in BC.

4.2. Chemistry of geopolymer concrete

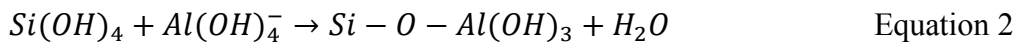
The chemistry of GPC encompasses the reaction of Al-Si source materials with an alkaline activator (NaOH+Na₂SiO₃ or KOH+K₂SiO₃) to form a polymeric chain and network structure, resulting in a hardened binder given in Equations 1-3. The chemistry behind geopolymer concrete is the following: First, the source materials are dissolved in the alkaline solution, breaking down the Si and Al atoms into free ions and small molecules. This occurs at high pH conditions facilitated by the alkaline activator. Second, the dissolved Si and Al species then undergo polycondensation, forming a three-dimensional aluminosilicate network. The reaction involves the condensation of silicate and aluminate oligomers. Finally, the

network grows, creating a solid, amorphous, semi-crystalline structure. This structure gives geopolymer concrete its strength and durability (Shehata et al., 2022).

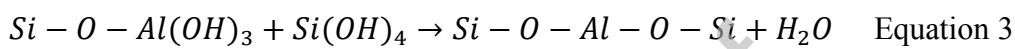
1. Hydrolysis of source materials:



2. Formation of oligomers:



3. Polymerization:



Compared to the OPC concrete composites, the mechanical and durability properties of cement composites having BC show appreciable improvement. BC, an environment-friendly and abundantly available material, has excellent potential to be replaced in cementitious composites. However, the primary concern is the dosage, as the maximum limit shall not exceed about 10%, as found in many studies. This is because of less CaO content in BC that results in less C-S-H gel formation at high dosages. There should be no alternative where the maximum substitution of BC can be promised to promote sustainable development. Fig. 5 to Fig. 7 in chemical properties (Section 2.3) show oxide composition in various types of BC specimens, confirming the availability of alumina and silica in an appreciable amount that is mandatory for material to be used as a precursor in geopolymer concrete. When dissolved in the alkaline solution, the finely grounded activated BC breaks down the Al and Si into free ions and small molecules. The dissolved Si and Al species then experience polycondensation, forming a three-dimensional aluminosilicate network. The reaction involves the condensation of aluminate and silicate oligomers. The network grows, creating a solid, amorphous, semi-crystalline structure, giving geopolymer concrete strength and durability. The decline in mechanical properties by increasing the BC dosage above the optimum range is due to porous structure and the disproportion in hydration process outcome between cement and BC, as the quantities of CaO and SiO₂ in BC are less than in cement. However, C-S-H gel is not accountable for hardening in GPC; it is C-A-S-H (calcium, alumina, silica, hydrate) gel that binds and gives strength to composites. The difference in hydration products will surely make a maximum substitution of BC in GPC possible.

4.3. Biochar as a binder in geopolymer composites

The growing interest in the use of BC as a partial alternative of cement in OPC since the last decade necessitates its use in GPC as an aluminosilicate source material. A few studies have been done in the past using biomass ashes in GPC. Rajamma et al. (Rajamma et al., 2012) investigated the effect of wood biomass substitution in FA-based and FA and metakaolin-based composites. They reported wood biomass show better strength while using in metakaolin based mortar than FA-based composite. Abdulkareem et al. (Abdulkareem et al., 2019) explored inclusion of wood ash partially in place of FA (10-30 wt.%) in GP mortars. The outcomes exhibited improvement in porosity and compressive strength up to 20% substitution of ash compared to reference FA-based GP mortar at 3 and 7 days, encouraging the development of C-S-H and C-A-S-H gel due to high calcium content, proving that the wood ash could potentially replace precursor materials, providing safe discarding of this waste. Silvestro et al. (Silvestro et al., 2023) produced geopolymer composite by adding wood ash (10 and 20 wt.%) in MK-based composites and presented that the specific surface area of ash influences the viscosity, yield stress, and reactivity of geopolymers. A comparable strength of 20 wt.% ash-based and reference MK-based composite was seen. Also, Fourier-transform infrared spectroscopy (FTIR) results support the occurrence of geo-polymerization reaction of MK with wood ash-based composite. A study conducted by Khamlue et al. (Khamlue et al., 2019) used MK and GP blends with BC based on aluminum oxide. They examined BC content at weights of 0, 10, 20, and 30% in the GP matrix. The liquid Na_2SiO_3 and NaOH at a precise quantity and molar ratio were used to speed up the geo-polymerization process. In addition, a 3.0% H_2O_2 solution was used as a blowing component. The material density increases dramatically with up to 30% BC content. It goes from around 0.80 g/cm^3 without BC to 1.25 g/cm^3 with 30% BC. Simultaneously, this addition decreased water adsorption from 83% to 35% and porosity from 67% to 45%, indicating BC's potential contribution to improving and enhancing the physical performance of the resultant GP.

4.3.1. Long-term performance

The use of BC performed remarkably well in cementitious composite and significantly improved their durability qualities by replacing a certain quantity of cement (Aneja et al., 2022; Yang and Wang, 2021). (Praneeth et al., 2021) concluded that 5 wt.% poultry litter BC decreased permeability, (Aneja et al., 2022) showed that the incorporation of rice husk BC 5 wt.% decreased permeability by 17.3%. This is due to the fine-sized BC diminishes voids while enhancing the hydration process (T. Chen et al., 2022). (Khan et al., 2021) suggested that 5 wt.% cement replacement with bagasse BC improved the sulphate attack resistance due

to the filler effect and internal curing by BC, less permeable structure increased resistance to sulphate attack. (Ling et al., 2023) found that the chloride ion penetration decreased by 32% by adding 3 wt.% waste wood BC in place of cement. (Zanotto et al., 2022) pointed out that the 5 wt.% BC incorporation into concrete composites reduced the risk of steel rebar corrosion, by reducing the access of oxygen to the rebars. The potential application of BC in GPC is attributed to its porous structure and moisture-retention capacity, which can improve the internal curing process of GPC (Shafie et al., 2012). This can mitigate issues such as shrinkage, cracking, permeability, acid, and chloride attacks, which are more common in conventional concrete over time. Under humid conditions, BC progressively releases absorbed moisture, facilitating a consistent hydration process, hence enhancing the material's long-term strength and durability (Xie et al., 2024). GPC often exhibits superior resistance to acidic assaults compared to traditional Portland cement concrete owing to its reduced calcium content (Rihan et al., 2024). Nevertheless, using BC with elevated silica concentration might enhance this resilience. The improved adhesion of aluminosilicate chains in geopolymer concrete, along with BC's capacity to raise matrix density, resulting in reduced permeability contributes to the mitigation of acid penetration. Long-term studies indicate that composites containing BC have reduced degradation rates in acidic conditions (Masud et al., 2023), hence maintaining structural integrity over time.

Reduced particle size improves compatibility with the matrix, diminishes voids, and enhances matrix density, hence aiding in the resistance to freeze-thaw damage. (Jia et al., 2023b) indicated that the incorporation of BC does not affect or improve the freeze and thaw resistance of concrete. The inclusion of 20 wt.% of BC remarkably increased relative residual compressive strength to 98%. This is due to the reason that the substitution of high-volume BC particles facilitates the creation of additional independent internal macropores, resulting in providing a larger surface area for frozen water to expand and ultimately restrained specimens from cracking (Sikora et al., 2022). The porous composition of BC will not adversely impact the freeze-thaw resilience of GPC as well. Integrating BC with precursors such as silica fume, fly ash, and slag augments matrix density and diminishes the occurrence of micro-cracks. These additives enhance the composite's freeze-and-thaw resistance by reducing permeability and restricting water intrusion which are the major causes of freeze-thaw degradation.

4.3.2 Thermal insulation properties

BC, with its porous structure, reduces heat transfer and will enhance the thermal insulation properties of GPC, making it an effective additive in high-temperature sites and fluctuating temperatures. (Lee et al., 2019) found that BC, when replaced with 10 wt.% cement, can significantly reduce thermal conductivity by 67.21% compared to plain mortars. According to the (Rodier et al., 2019), incorporating 6% bagasse BC into the concrete mixture resulted in a 45% decrease in thermal conductivity. (Sikora et al., 2022) included 20 wt.% BC and observed 28% decrease in thermal conductivity compared to ordinary concrete. (Akinyemi and Adesina, 2020; Yun et al., 2013) and (Akinyemi and Adesina, 2020) demonstrated that incorporating BC into cementitious composites interrupted the thermal bridge, serve as a barrier for heat transfer within the matrix, resulting in reduced thermal conductivity. BC's stable carbon structure enhances GPC's heat resistance, minimizing thermal degradation risk and its pyrolysis-generated nature will allow the composites to maintain structural integrity even at high temperatures. When combined with GPC, can help absorb and release heat, reducing thermal stresses, reducing microcracking risk, and extending the material's lifespan in regions with significant temperature changes. The BC-based GPC can enhance thermal insulation, enhancing energy-saving capacity in building construction, and benefiting structural designers by requiring less energy to maintain the structure's temperature (Praneeth et al., 2021), which ultimately work towards sustainable goals.

4.3.3 Carbon sequestration potential

BC is generated through the pyrolysis of biomass in environments without oxygen, leading to a stable material that is rich in carbon and does not degrade with time. Researchers showed that BC possesses significant potential for carbon sequestration, and its incorporation into cementitious composites may serve as an environmentally friendly approach to developing low-carbon materials. (Ying Zhang et al., 2022) concluded that 1-tonne biomass at 700°C pyrolysis could capture 980 kg CO₂eq. (T. Chen et al., 2022) found that 5 wt.% replacement of cement with BC saved 32.4 kg/m³ CO₂. (Gupta and Kashani, 2021) demonstrated 0.950 CO₂eq emissions using 3 wt.% of BC in place of cement compared to 1.002 CO₂eq emissions without the use of BC. The Intergovernmental Panel on Climate Change (IPCC) recommended BC as a potential material for carbon neutrality since its life cycle analysis (LCA) demonstrated that 1 tonne of BC can stabilize 2.0–3.3 tonnes of CO₂eq (Masson-Delmotte et al., 2022). When considering the carbon-trading credit, BC uses as a portion of aggregate in concrete stored up to 59 kg CO₂ per tonne, yielding a profit of 35.4 USD/m³ (Zhu et al., 2023). The incorporation of BC into GPC will effectively sequester carbon within

the matrix. The incorporation of this extra sequestration, along with the already diminished carbon footprint of geopolymer binders, positions BC-GP composites as a viable option for sustainable construction (Wang et al., 2023).

4.3.4. Economic viability

BC is more expensive than GGBFS or FA because it needs pyrolysis, but its performance and environmental benefits may offset the expense in some applications. The improved carbon sequestration, internal curing, and lower heat conductivity make BC more sustainable and ideal for high-performance applications that need durability, sustainability, and insulation (Lee et al., 2019; Wang et al., 2023; Ying Zhang et al., 2022). BC may minimize dusting, a problem with fly ash and silica fumes. Silica dusting causes respiratory problems, therefore eliminating silica-rich additives like silica fume can improve construction worker health (Hesse, 2018). Also, the continuous decrease in the production of FA and GGBFS does not guarantee the large-scale adaption of geopolymer composites (Assi et al., 2020a). Biochar particles are more stable and less likely to fly during mixing and handling, lowering worker dust exposure. Its particle structure improves concrete mix cohesiveness, minimizing dust-causing loose particles and making it a better choice for air quality and worker safety than silica or ash particles. BC along with GGBFS and FA can be mixed to maximize their benefits considering its potential for thermal stability and carbon sequestration making it a realistic and cost-effective augmentation in GP applications.

4.4. Biochar as an alkaline activator in geopolymer concrete

The highly alkaline character and existence of a significant extent of potassium oxide (K_2O) in most of the agricultural waste's BC promised the feasibility of use as an alkaline activator. Thomas et al. (Thomas et al., 2021) comprehensively reviewed the studies and trends in waste biomass ash-based concrete and established the viability of consuming biomass ashes from rice straw, banana leaf, elephant leaves, date palm, bamboo leaves, plantain peels, olive straw, wheat straw, and corn cob as alkaline activator based on their chemical compositions. Even though biomass ash includes a significant content of soluble alkaline amalgams (Vassilev et al., 2010), only three papers have been published on the possible use of agricultural wastes as an alkaline activator to date. Font et al. (Font et al., 2017) used olive stone biomass ash OBA (rich in K_2O and CaO content) in slag-based geopolymer mortar composites. The results showed a high alkalinity of BC in a water medium. The compressive strength reached 30 MPa after 7 days of curing at 65 °C which is superior to conventional (using KOH as an alkaline

activator) geopolymer mortar composites, using a 100% waste-based OBA alkaline activator. Alonso et al. (Alonso et al., 2019) performed physical, chemical, mineralogical, and radiological characterization of olive biomass fly ash (OBFA) and bottom ash (OBBA) in FA-based and slag-based geopolymer mortar composite. The 30 wt.% addition of OBFA in slag-based composites (70 wt.%) showed comparable compressive strength to paste activated by commercial KOH. However, 30 wt.% addition of OBFA or OBBA in FA-based composite proved ineffective since pH was not sufficient to activate the precursor. Also, biomass addition conformed to European legislation on protection against exposure to ionizing potential. The pyrolysis process increases the alkaline character of biomass which will surely make the addition of BC as an alkaline activator viable in FA-based geopolymer composites as well (Boakye et al., 2023; Rahman et al., 2023b). Peys et al. (Peys et al., 2016) incorporated maize stalks and maize cob ashes in MK-based geopolymer composites and concluded that 30-32 wt.% of K_2O was present in ashes, resulting in a pH of 13-14 after mixing with water. A compressive strength of 40 MPa was achieved with one part ash-MK blend. There is a strong possibility to use agricultural waste in GPC after pyrolysis, which may result more improvement in mechanical and durability properties.

4.4.1 Cost efficiency and performance

BC (rich in silica and highly alkaline character) is a cheap, renewable substance from biomass waste, making it a sustainable alternative to energy-intensive commercial alkaline activators. Its production through pyrolysis leads formation of bio-oil (potentially be utilized as a transportation fuel in place of diesel and heavy fuels (Shubhi Gupta et al., 2021)), and syngas (can be used in gaseous biofuel, and reaction atmosphere in thermal processes (Zhang et al., 2023)). The cost associated with producing BC showed considerable variation depending on the specific type, the source of the feedstock, and the scale of production (Akhtar and Sarmah, 2018; L. Chen et al., 2022c), typically varied between 378-557.85 USD/tonne (Fawzy et al., 2022) which is far less than the cost of conventional commercial alkaline activators sodium silicate (400 USD/ tonne) and sodium hydroxide (1000 USD/ tonne) (Abdollahnejad et al., 2015). The production of BC by pyrolysis is economically viable when weighed against the value and use of the byproducts. Although effective, the economic feasibility concerns for traditional activators limit the broad-scale adoption of GPC. Alkalinity for geo-polymerization can come from potassium and calcium oxides present in BC. The alkalinizing potency may not yet equal highly refined commercial activators but can partially be replaced by conventional activators without compromising cost and sustainability. BC as an activator

may not increase GPC strength immediately, but it can improve its durability and microstructure because of its porous structure, permeability, and chemical resistance nature (Gupta and Kashani, 2021). Its alkalinizing action is enough to start and sustain geopolymerization, especially when coupled with fly ash or slag, which strengthens the aluminosilicate network and ultimately increases the mechanical and durability properties of the composite (Elgarahy et al., 2023).

4.5. Production of biochar-geopolymer concrete composites

4.5.1. Inclusion methods

The methods used to incorporate BC in GPC hold the key to a potential revolution in the construction industry. These approaches provide distinct benefits and concerns based on the required goal and the features of BC and GPC. Table 11 describes some important methods used by researchers in the past to include BC in concrete. By examining the procedures and advantages of different methods, the strategy can be made to add BC to GPC.

Table 11: Biochar inclusion methods and their advantages in concrete products.

Methods	Procedure	Advantages	Reference
Dry mixing	Directly incorporate the biochar into the GPC dry mix. To get the best dispersion and avoid particle agglomeration, thorough mixing is necessary.	The particles are evenly distributed throughout the mixture.	(Gupta and Kua, 2018)
Wet mixing	Pre-wet biochar particles are mixed with other wet ingredients to create a homogeneous blend.	It promotes stronger bonding and improves biochar's compatibility with the other matrix elements. The performance of the substance is enhanced by uniform distribution.	(Lu et al., 2014)
Slurry mixing	Prepare biochar-water slurry, then add it to the GPC mix.	Improves the dispersion of biochar inside the GPC matrix. improves the composite's overall performance and characteristics.	(Yuying Zhang et al., 2022b)
Surface	Apply a thin coating of	Strengthen the connection between	(Maljaee

coating	polymers onto the surface of BC particles.	the biochar and the adjacent matrix to produce a cohesive and well-integrated composite.	et al., 2021a)
Pelletization	Compresses biochar particles into homogeneous pellets or granules of particular size.	Guarantees a steady and regulated distribution of particle sizes, promoting their even dispersion throughout the mixture. The strength, durability, and structural integrity of GPC are improved.	(Bazargan et al., 2014)
Pre-activation	It involves treating biochar (chemical activation or exposure to high temperatures) before incorporation into the GPC mix.	It changes the surface characteristics of biochar, increasing reactivity and adsorption capacity.	(Akhil et al., 2021)

The Taguchi approach (Ntemi et al., 2022), and response surface methodology (RSM) (Gaitonde et al., 2012), can fast-track BC dose determination without substantial trial and error. Researchers are concurrently optimizing BC dose, particle size, and other mix components using these methods, minimizing the time needed to find ideal formulations (Egodagamage et al., 2023; Nusrat Aman et al., 2023). Moreover, the short-term performance metrics can assess the contribution of BC dosage instead of long-term testing. This includes early compressive strength, setting time, workability, and water absorption rate may be tested quickly after casting to assess BC's influence on GPC. BC dose depends on application needs (e.g., structural vs. non-structural), but past research has indicated that 2–10 wt.% of binder is a good compromise between strength increase and durability without compromising workability in concrete applications (Aneja et al., 2022; Aziz et al., 2023; Barbhuiya et al., 2024; Haris Javed et al., 2022; Jia et al., 2023a; Ling et al., 2023; Restuccia et al., 2020). The further increase in dosage compromised the C-S-H gel formation that is responsible for matrix hardening (Cunningham and Keane, n.d.). The binding product in geopolymer composites is C-A-S-H instead of C-S-H, where more proportion of BC can be adjusted. Machine learning methods (Sun et al., 2022) might analyze massive datasets of mixed design factors and

performance outcomes to forecast biochar dosage in the future. Researchers may use prior data to teach computers to accurately propose BC doses for desired qualities, avoiding the need for detailed physical testing.

In conclusion, the process of adding BC to GPC is important and depends on several variables: including the intended use, the desired qualities, the ratio of liquid-to-binder, the molarity of basic solution, etc. Selecting the best technique is crucial to guaranteeing that the BC is well-distributed and efficiently used in the GPC mix.

4.5.2. Biochar selection

Several aspects must be considered when selecting BC for use in concrete applications to assure suitability with the cementitious medium and to maximize the required qualities of the final BC-GPC product. Fig. 16 illustrates essential factors while selecting BC for concrete usages.

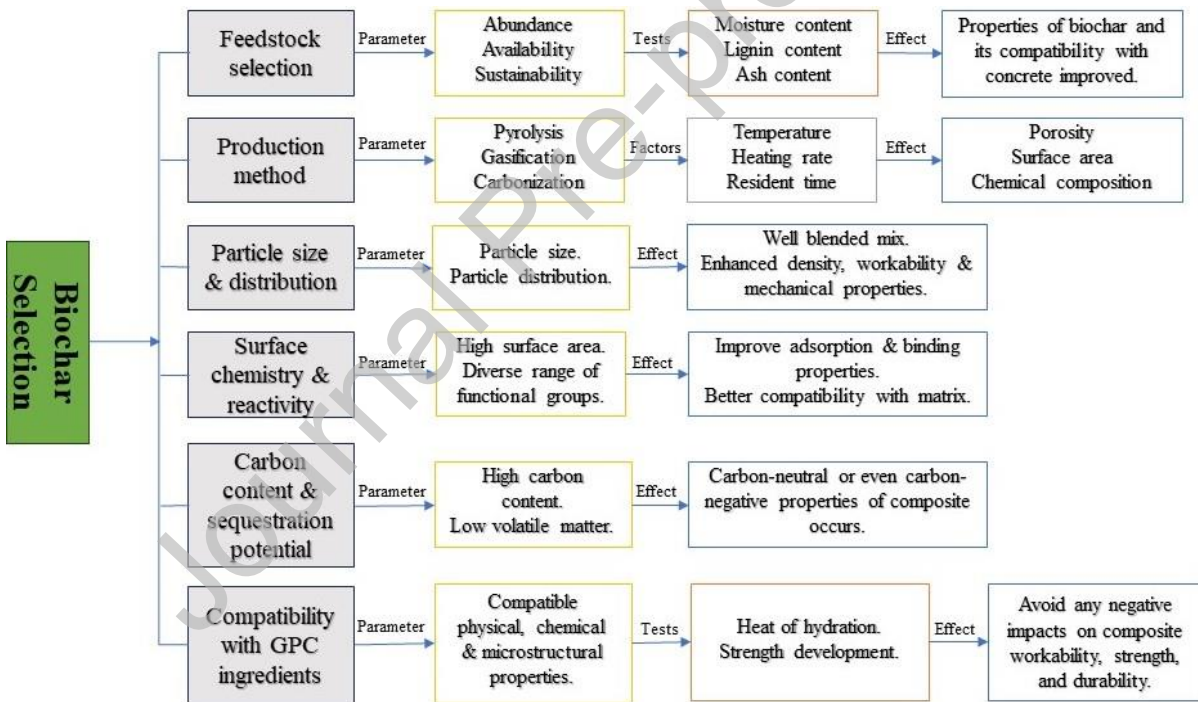


Fig. 16: Key considerations while choosing biochar for GPC (Bird et al., 2011; Bolan et al., 2022; Leng et al., 2021; Maljaee et al., 2022; Tan et al., 2021).

To summarize, careful consideration for surface area, porosity, chemical composition, particle size, pH level, activation status, and moisture content of BC through extensive testing and assessment must be ensured before BC's use in concrete composites. This will guarantee the targeted results, such as enhanced mechanical characteristics, increased sustainability, and

carbon sequestration capability to decrease environmental influence and create an ecological future.

4.5.3. Mixing and curing protocols

The use of BC has demonstrated the ability to expedite the setting process, hence enhancing production efficiency (Senadheera et al., 2023). The efficient and thorough mixing is necessary to prevent premature stiffness due to the faster setting that occurs with BC incorporation. To avoid letting the mixture solidify before placing, it may be necessary to slightly shorten mixing times to properly spread the BC or use the appropriate admixture that will slow the hardening process. Also, to make sure that the BC is well distributed throughout the geopolymer matrix, and that the performance is constant from batch to batch, a high-shear mixer could be useful. Research conducted by (Barbhuiya et al., 2024) indicates that appropriate mixing equipment and procedures are essential for attaining a uniform matrix in BC-modified mixtures, particularly with rapid-setting materials. The reduced setting time can influence curing methods, particularly if the combination attains the initial set more rapidly. Curing conditions in geopolymer concrete, particularly temperature and humidity, are critical for attaining maximum strength. A marginally altered curing method, such as initiating curing immediately after mixing or employing ambient curing at an elevated temperature, might facilitate efficient geo-polymerization while tolerating the accelerated setting. In practical manufacturing, BC's capacity to expedite setting may improve productivity and minimize delays, which is advantageous in prefabrication or on-site applications with constrained timelines. The altered setting and curing durations necessitate vigilance in quality control to guarantee that the concrete's structural integrity remains intact despite expedited handling.

4.6. Quality control and testing

Quality control and testing are fundamental to ensure the performance and trustworthiness of the BC-GPC composite. Thoroughly testing BC's quality and characteristics before incorporating it into concrete is crucial. Some important tests on BC to ensure its compatibility with GPC are shown in Table 12. Fig. 17 shows important considerations for testing BC-GPC composites.

Table 12: Important tests ensuring the suitability of biochar with geopolymer mixing and production.

Property	Testing method	Purpose	Reference
Surface area and	BET (Brunauer-Emmett-	Determine surface	(Brunauer et al.,

porosity	Teller) analysis. (ASTM D3663)	area and porosity.	1938; “Standard Test Method for Surface Area of Catalysts and Catalyst Carriers 1,” n.d.)
Chemical composition	X-ray fluorescence and X-ray diffraction analysis (ASTM C114, ASTM D934)	Measure the content of silica, alumina, and other elements.	(<i>Standard Practices for Identification of Crystalline Compounds in Water-Formed Deposits By X-Ray Diffraction 1</i> , n.d.; <i>Standard Test Methods for Chemical Analysis of Hydraulic Cement 1</i> , n.d.)
Particle size distribution	Laser diffraction or sieve analysis (ISO 13320, ASTM C136)	Determine particle size distribution.	(“Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates 1,” n.d.)
pH level	pH meter or pH paper (ASTM D4972)	Measure the biochar’s pH to ensure compatibility with the alkaline environment of GPC	(“Standard Test Methods for pH of Soils 1,” n.d.)
Moisture content	Oven drying method. (ASTM D4442)	Measure the moisture content of the biochar.	(“Standard Test Methods for

			Direct Moisture Content Measurement of Wood and Wood-Based Materials 1 Method A- Primary Oven-Drying Method Method B- Secondary Oven-Drying Method Method C- Distillation (Secondary) Method Method D-Other Secondary Methods. Sections Method A- Primary Oven-Drying Method 5 Method B- Secondary Oven-Drying Method 6,” n.d.)
Thermal analysis	Thermogravimetric analysis (TGA) (ASTM E1131)	Assess thermal stability and composition.	(“Standard Test Method for Compositional Analysis by Thermogravimetry 1,” n.d.)
Microscopic analysis	Scanning electron microscopy	Observe the microstructure and	(International and American Society

	(ASTM E766)	surface morphology.	for Testing, n.d.)
Adsorption capacity	Iodine or methylene blue adsorption tests (ASTM D4607)	Evaluate the adsorption properties of the biochar.	(“Designation: D4607 – 14 Standard Test Method for Determination of Iodine Number of Activated Carbon 1,” n.d.)

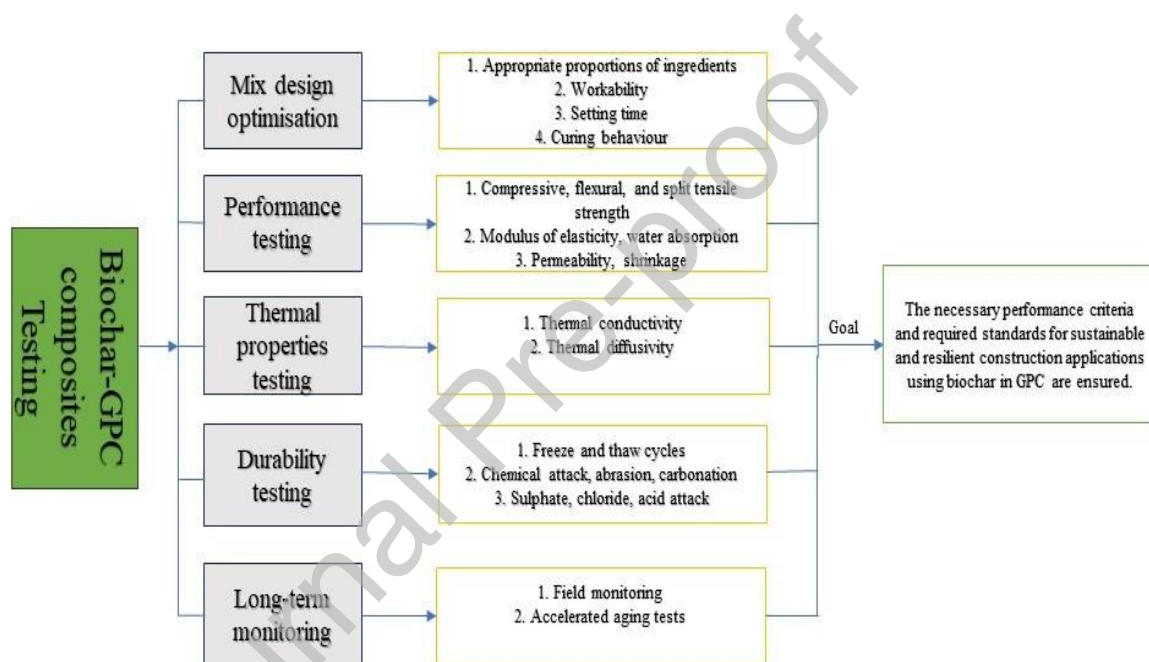


Fig. 17: A schematic chart of key considerations for testing of Biochar-GPC concrete (Aziz et al., 2023; De Carvalho Gomes et al., 2022; Souradeep Gupta et al., 2021a; Mishra et al., 2023; Praneeth et al., 2020; Singhal, 2023; Sirico et al., 2021; Tan et al., 2022; Yang and Wang, 2021).

The quality, performance, and durability of BC-GPC may be effectively assessed and guaranteed by the strict implementation of quality control protocols and the careful execution of comprehensive testing. Effective implementation of these methods is crucial to fully harness the ecological capabilities of BC as a construction material, while also ensuring the highest standards of safety and reliability. By implementing stringent quality control

measures, the building industry may embrace BC-GPC as a viable and environmentally friendly option to foster a more sustainable future.

5. Challenges and future perspectives

5.1. Challenges and Limitations

The challenges of using BC in GPC stem from its unique properties (high porosity leading to reducing strength and durability, heterogeneous composition because chemical composition depends on feedstock, low density can impact the mechanical and workability properties, pH variability can affect the alkaline environment needed for geo-polymerization, carbon reactivity with alkaline activator solutions, high water demand because of high surface area and porosity leading to workability and curing issues, variation in thermal stability can affect long term durability issues, etc. The behaviour of BC with polymerization reaction is important to consider and ensured through chemical composition analysis (XRF, XRD), microstructural analysis (SEM, EDS), FTIR, TGA, DSC, Calorimetric analysis, etc. While being a sustainable material, BC's interaction with GPC must be carefully evaluated by conducting life cycle assessments (LCA) to ensure it does not introduce negative environmental impacts. There is no study on the use of BC in GPC, but considering the issues of BC in cementitious composites, the following are the key challenges associated with BC use in GPC that must be solved while incorporating BC in GPC given in Table 13.

Table 13: Key challenges of using biochar in geopolymer concrete and their solutions.

Challenge	Description	Result	Solution
Inconsistent composition	Varies widely based on the type of biomass used and pyrolysis conditions.	Variability in the properties of GPC.	Use biochar from a consistent, well-characterized biomass source. Maintain pyrolysis conditions (temperature, time, and atmosphere). Mix biochar from different batches to achieve uniform properties.
High carbon content	Affects the chemical	Inhibit the formation of the	Using biochar in proportional increments of 10% up to 100% in

	reactions during geo-polymerization.	geopolymer network.	place of conventional Al-Si sources and checking the properties for each percentage to report optimum content.
Porosity and water absorption	Highly porous and can absorb a significant amount of water.	Alter the water-to-solid ratio in the mix, affecting the workability and strength of GPC.	Pre-saturating the biochar or adjusting the mix design to account for the water absorption.
Alkali reactivity	Contains organic compounds that react with the alkaline activator solution.	Interfere with the geo-polymerization process.	Pre-treating biochar (washing, acid/base treatment, thermal/chemical activation, grinding) to remove impurities, modify surface chemistry, and increase surface area, particle size, and reactivity.
Mechanical properties	Influence the mechanical properties of geopolymer concrete.	Decrease in compressive, tensile, flexural strength, and modulus of elasticity.	Optimizing the biochar's amount and understanding its impact through experimental testing.
Chemical stability	Contain impurities or residual organic matter.	Affects the long-term chemical stability of GPC.	Try to ensure biochar's purity through its use from reputable suppliers, inspecting it visually, and conducting chemical and microstructural analysis.

5.2. Future research and development opportunities

Using BC in GPC offers great research and improvement possibilities to investigate the potential advantages as a sustainable alternative in GPC production, ultimately promoting sustainability. Some essential fields of emphasis for upcoming studies comprise:

1. Standardizing the feedstock and pyrolysis parameters (heating rate, pressure, residence duration, etc.) is required to create BC that satisfies GPC's chemical and physical requirements. It is advised to inspect the effects of various biomass feedstocks on the mechanical, chemical, and physical characteristics of BC by adjusting the pyrolysis conditions; in the end, this will determine the fresh, mechanical, and durability features of GPC made with BC.
2. A thorough microstructural and chemical research is required to optimize the geo-polymerization reaction by studying the interaction between BC and the alkaline activators used in conventional GPC. Also, it is required to explore various pre-treatment methods for BC to remove impurities and reduce reactivity that could interfere with the geo-polymerization.
3. Researching the development of optimized mix designs that include BC while sustaining or improving the engineering properties of GPC is of utmost importance. It is recommended to examine the use of nano- and micro-scale BC particles partially or completely to improve the structural integrity of the GPC.
4. Researchers should emphasize conducting comprehensive life cycle assessments (LCA) to assess the eco-friendly benefits and impressions of consuming BC in GPC, including carbon sequestration potential and quantification of potential reductions in carbon footprint compared to traditional GPC. The input variables may include BC production processes, biomass type, transport emissions, raw materials (e.g., FA, MK, slag, etc.), and alkaline activators (NaOH/KOH, Na₂SiO₃/K₂SiO₃, etc.).
5. It is important to perform thermal stability and fire resistance of BC-enhanced GPC to determine its suitability for high-temperature applications and thermal insulation. This will make it suitable for energy-efficient buildings.
6. Cost-effectiveness and scalability: Research attempts must focus on developing cost-effective and scalable BC-GPC manufacturing systems. By refining the BC manufacturing process and its substitution in GPC, we may increase BC's economic feasibility as a sustainable building material while reducing the environmental impacts.

6. Conclusions

In conclusion, biochar has a high potential for usage in cementitious composites (OPC and GPC) to promote green construction methods. BC, a carbon-rich substance gained from

biomass, has various advantages, including lower carbon footprints, enhanced material fresh and hardened qualities, the ability to use waste on a wider scale, and contribution to the circular economy. This review leads to the following conclusions:

- There is a decrease in the production of fly ash, and the pollution caused by the expensive and not readily available alkaline activator solutions necessitates the use of a continuous waste that can serve as an appropriate substitute for fly ash in geopolymer concrete. Biochar has the potential to be used as an alkaline activator and as an aluminosilicate source in geopolymer concrete. Geopolymer concrete can be made by using different agricultural wastes (e.g., biochar).
- The physical and chemical properties of biochar such as yield, surface area, pH, density, particle size produced through pyrolysis can be controlled by monitoring pyrolysis pressure, temperature, heating rate, and resident time. In this way, biochar can be engineered to meet the target requirements as an aluminosilicate source for geopolymer concrete.
- In normal OPC concrete, biochar is being used in a small proportion (up to 5% volume) as a filler material that can improve the mechanical and durability properties due to its angular, flaky, and rough surface characteristics. However, in geopolymer concrete, a high volume of biochar can be used since the role of biochar in geopolymer is different from the role of biochar in OPC concrete.
- A biochar made from agricultural wastes (rich in silica and alumina) offers a feasible alternative to traditional precursors for geopolymer composites (alumina-silica source such as fly ash, metakaolin, slag, etc.). Aluminosilicate monomers are necessary for polymerization process.
- Biochar derived from agricultural waste, high in potassium and calcium oxide, can be utilized as an alkaline activator solution when mixed with water. The presence of potassium oxide accounts for the highly alkaline character of the water.

In summary, geopolymer concrete incorporating biochar could contribute to the development of sustainable concrete, achieving circular economy and net zero emissions.

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Declaration of interests

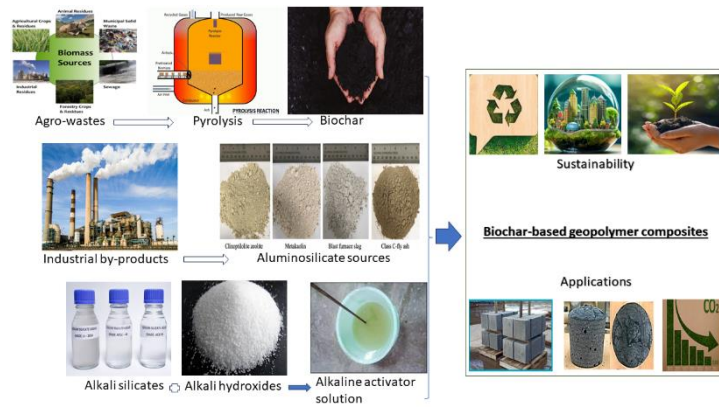
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

None

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