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Low carbon biochar amended fly ash–cement building blocks: Assessment of metal leaching scenarios

Sai Praneeth^{1,3}, Sanandam Bordoloi² and Ajit K. Sarmah^{1*} 

Abstract

Demolition cementitious waste poses significant environmental challenges at the end of its lifecycle. To address this, fly ash (FA), a highly leachable material and a supplementary cementitious material, was combined with biochar (BC) to produce eco-friendly mortar bricks with reduced carbon emissions and contaminant leaching. BC was incorporated at 2%, 4%, and 6% by weight, and the resulting blocks achieved compressive strengths of 8–12 MPa after 28 days, meeting Eurocode 6 standards for use in harsh conditions. Leaching tests under synthetic precipitation showed reductions in Al, Se, Ba, and Cr concentrations by 72%, 48%, 58%, and 53%, respectively, with 6% BC. While Al remained above drinking water limits, Cr levels dropped below limits when BC exceeded 4%. Leaching followed typical pH-dependent behaviour: Al exhibited an amphoteric trend, and Cr showed an oxyanionic trend, with minimal leaching at neutral pH. This study highlights the role of BC in reducing leaching potential in cementitious composites and provides critical data for geochemical modelling in sustainable demolition waste management systems.

Highlights

- Biochar addition to 2% fly ash replacement can increase strength by pore-filling.
- Al, Se, and Cr SPLP concentrations in blocks were above the drinking water regulations.
- The SPLP Cr concentrations for blocks can be reduced to 53% with 6% biochar addition.
- The Al and Cr concentrations showed oxyanionic pattern as a function of pH.
- The TCLP results for leached elements from fly ash confirmed non-hazardous classification.

Keywords Biochar, Fly ash, Contaminant, Leaching test, Leachability, Mix design

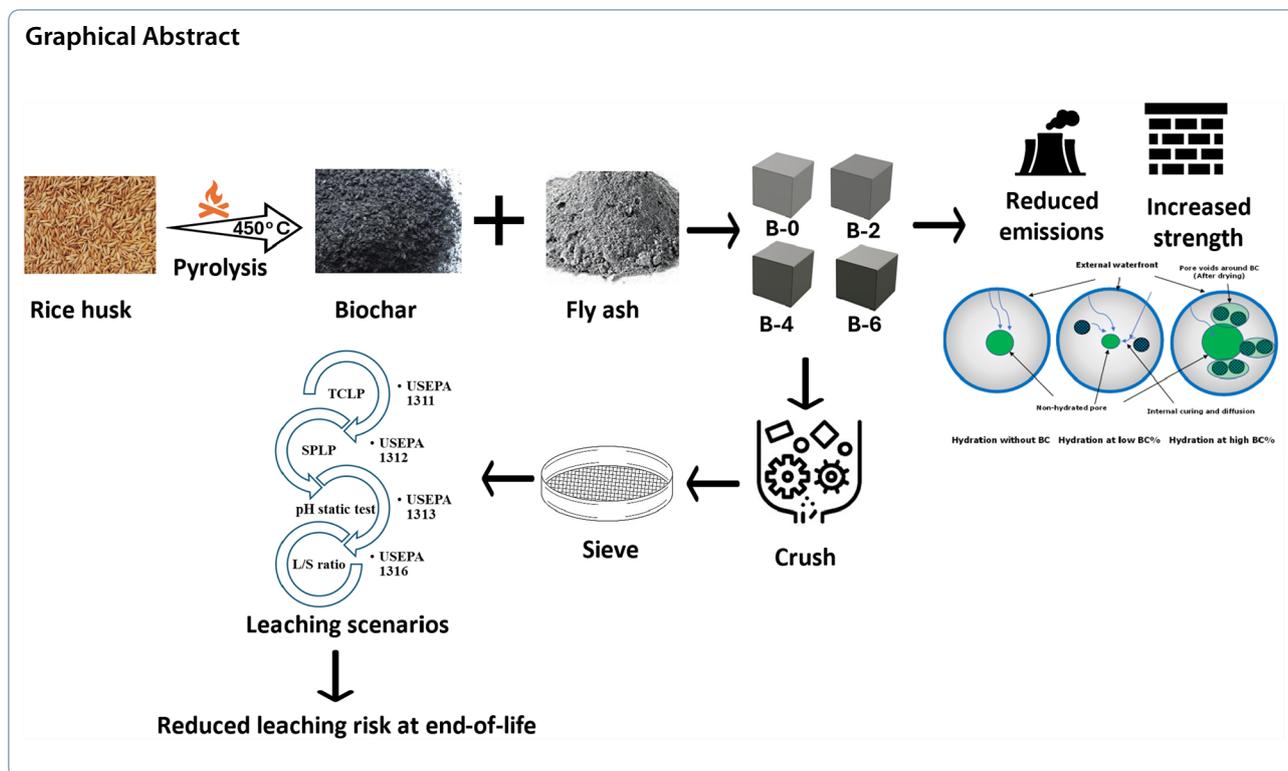
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1 Introduction

Portland cement production generates 950 kg of CO_2 per tonne, accounting for 8% of global CO_2 emissions from over 4 billion tonnes produced annually (McDonald et al. 2022). The European Commission targets a net reduction in greenhouse gases by 55% before 2030 and ultimately aims to achieve net-zero CO_2 emissions by 2050 (Wang et al. 2021). This goal in the construction sector can be achieved through reducing the usage of low CO_2 emission materials such as Portland cement, utilizing secondary cementitious materials (SCMs) to improve hydration, or utilizing materials that can improve long-term natural carbonation for strength gains (Chaudhury et al. 2023). Among the SCMs, coal combustion residue generated during the coal combustion process in thermoelectric power plants is one of the most utilized SCMs in the construction sector. Fly ash, constituting a significant portion of these residues (ACAA, 2021), is widely used in construction materials as an SCM for high to low-load-bearing building infrastructure. Globally, China is the largest producer of fly ash (~ 600 Mt in 2018), with 3 billion tonnes of fly ash stockpiled in landfills (Luo et al. 2021), followed by India (227 Mt in 2019–20) (CEA, 2019) and EU (88 Mt) (ECOA, 2020). Despite production and availability in large quantities in the construction industry, the global utilization of fly ash remains around 42–63% (Han et al. 2021), and most

unutilized fly ash remains as legacy fly ash ponds. Even though coal combustion residues are planned to be eventually phased out, most of them remain unutilized across the globe. FA being highly leachable, improper land disposal can potentially cause heavy metal leaching into the surrounding land and water bodies. It is reported that 1.5–36.4% of total available concentration can be potentially extractable under leaching conditions (Neupane and Donahoe 2013; Fernández et al., 1994). When used in low quantities in mix design for load-bearing structures, the encapsulated FA may lower the risk of leaching during the working period (Ayorloo et al. 2022). In general, the usage of FA in masonry blocks ranges between 50 to 70% (Naganathan et al., 2015; Abbas et al. 2017), which has high susceptibility to leaching. However, end-of-life disposal and reuse as construction demolition waste of high FA building blocks may likely lead to leaching-related environmental problems. The leaching scenarios can be further exacerbated in disposal scenarios such as marine environments (acidic environments), extreme rainfall conditions (different solid to liquid conditions), and changing landfill pH with age (Statom et al. 2004).

To further minimize the CO_2 footprint, the use of supplementary cementitious materials (SCMs) and SCM-based building masonry units has been investigated, with Portland cement being incorporated at very low levels (< 10%) (Raut et al. 2011). Recently, the addition of biochar (BC) as

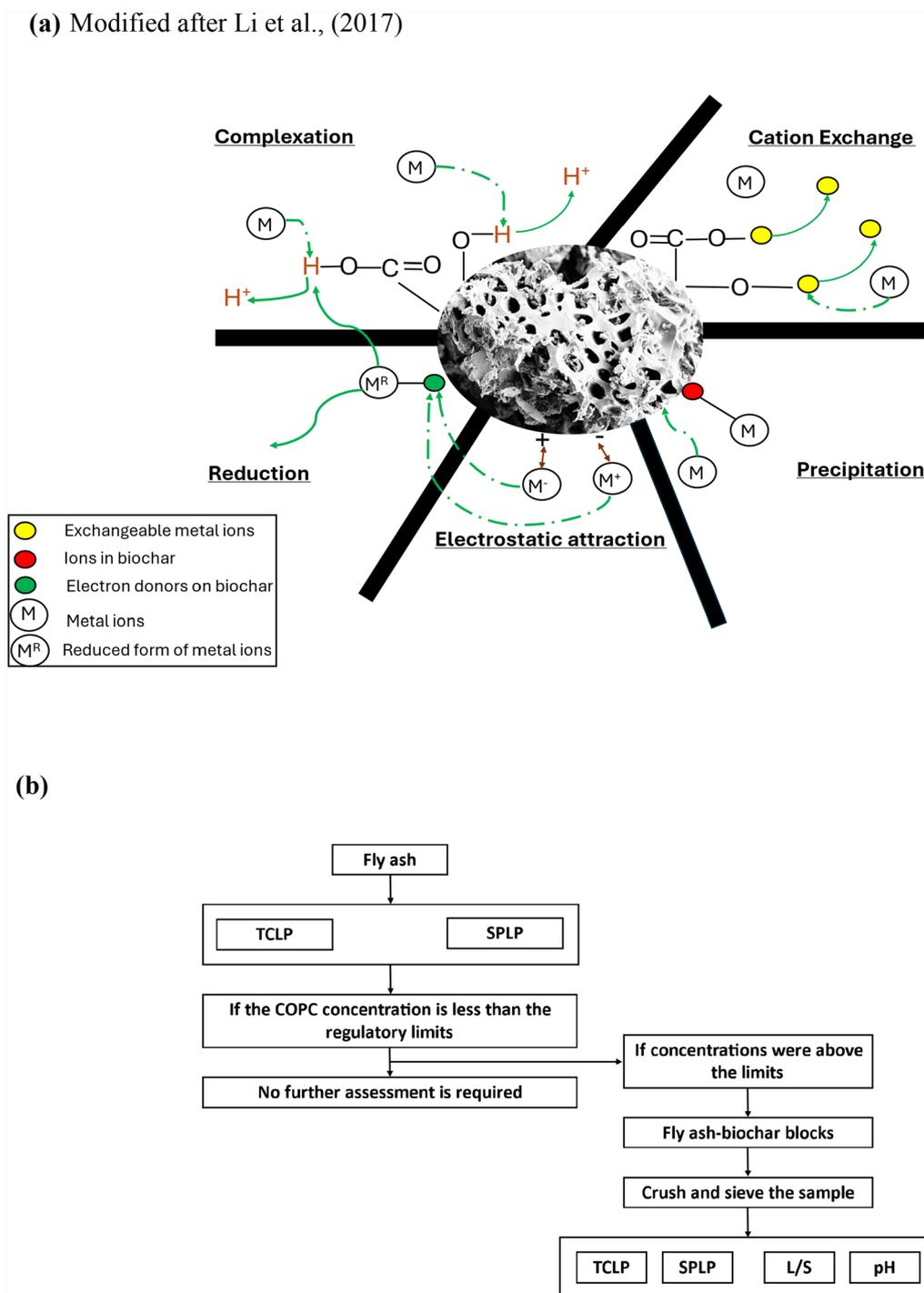


Fig. 1 Retention mechanisms of common metals by BC (a). Leaching assessment framework (b)

a filler material has also been explored. BC is the solid by-product of the pyrolysis process following the thermal degradation of organic biomass. It has been reported that BC can bind 2–3 times more CO₂ compared to its weight due to its high porosity and affinity for non-polar compounds

(Fig. 1a) and is considered by the International Panel for Climate Change (IPCC) as one of the most promising approaches to permanently removing carbon from its cycle (Wang et al. 2021). Under room temperature, unmodified BC has been reported to capture between 20 and 73.5 mg

Table 1 Elemental oxides of FA

Oxides	SiO ₂	Al ₂ O ₃	TiO ₂	MnO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	CaO
Composition (%)	39.97	18.41	1.25	0.09	9.8	4.8	0.38	0.67	0.18	21.1

CO₂ per gram of BC (Kua and Tan 2023), which also contributes to the long-term strength gains through carbonation. BC properties are highly dependent on the pyrolyzed organic feedstock and the pyrolyzing conditions. Although recent studies (Praneeth et al. 2020; Gupta et al. 2021; Mishra et al. 2023) have explored the physical and chemical properties of fly ash (FA) and biochar (BC) in the development of low CO₂-intensive building blocks, the potential metal leaching issues arising from these cementitious composites have been hitherto neglected and thus warrant investigation.

BC is considered to be one of the most eco-friendly adsorbents for metal leaching and the established mechanisms for metal retention is schematically described in Fig. 1a. The major mechanisms consist of complexation, cation exchange, precipitation, electrostatic attraction, and reduction (Bartoli et al. 2020). It is likely that at the end-of-work life cycle, the presence of BC might lower the leaching expected from a traditional FA-based demolition waste based on the conditions of its disposal. During transport, reuse, and dumping scenarios, when the fly ash particles come in contact with moisture in any form such as precipitation, moisture content, etc. the heavy metals could leach to the surrounding water bodies and may potentially contaminate the environment.

Leaching is a very complex phenomenon affected by various factors such as physical factors (time, flow rate, temperature, and particle size, etc.), chemical factors (pH, kinetics, liquid to solid ratio (L/S), complexation, etc.), biological factors, etc. (Kosson et al. 2017). Toxicity Characteristic Leaching Procedure (TCLP) (USEPA method-1311, 1992) and Synthetic Precipitation Leaching Procedure (SPLP) (USEPA method-1311, 1992) are considered basic characterization tests, defined under USEPA 1311 and USEPA 1312. The TCLP test is used to classify the waste sitting on a landfill as hazardous or not whereas SPLP is designed to create precipitation scenarios in the laboratory conditions and compare the leachate data to drinking water standards. But from a specific decision-making perspective, the data related to L/S, time, and pH are some of the important factors that need to be considered by the regulatory bodies (Hattaway et al. 2013). USEPA method-1313, (2012) describes the leaching scenarios under differing pH values, while USEPA method- 1314. (2013) specifies the leaching scenarios under different liquid to solid ratios.

This research, to the best of our knowledge is the first of its kind that mainly focuses on creating low-carbon

building blocks using biochar (BC) and fly ash (FA), with only 2% Portland cement included in the mix. This study tested two hypotheses. First, the addition of biochar enhances the compressive strength of fly ash–cement blocks by improving pore structure and internal curing. Second, biochar effectively immobilizes heavy metals in fly ash-based demolition waste, thereby reducing leaching risks under diverse environmental conditions. We explored various mix designs with differing BC contents to develop these eco-friendly blocks. The overarching objective was to evaluate the mechanical strength of the resulting blocks and subsequently investigate their potential for metal leaching. Specifically, we set out to assess the mechanical strength of these blocks and investigate their metal leaching potential. Leaching behavior was rigorously examined using batch studies, including the Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), and other EPA-regulated methods. Advanced analytical techniques were used to compare contaminant concentrations against permissible drinking water limits, offering new insights into the mechanical and environmental performance of BC-FA blocks. We envisaged that the findings obtained from this comprehensive structural and environmental testing of building blocks developed using BC and fly-ash would pave way and highlight their potential use as innovative, sustainable alternatives for construction practices while simultaneously addressing environmental concerns.

2 Materials and methods

2.1 Materials

The fly ash used in this current study was generated in the Huntly power station, New Zealand, and purchased from the Golden Bay Cement, New Zealand. The elemental oxide composition of the fly ash is summarised in Table 1, and the fly ash was stored in air-sealed containers prior to its use. The cement used was inspected to be free of lumps and moisture for use in building blocks. Rice husk biochar (BC) was produced through slow pyrolysis at 500 °C by Oliver Enterprises Philippines in an oxygen-free environment. After production, the biochar was ground to reduce its particle size before being used in block manufacturing. Its chemical composition primarily includes silicon (25%), along with trace amounts of potassium (1.20%), calcium (0.5%), and iron (0.04%), making it a suitable silica-rich supplementary material. The fly ash's oxide composition was found using X-ray Fluorescence Spectroscopy (XRF).

The composition of biochar was determined by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo Scientific, Waltham, MA, USA) and an elemental analyzer.

2.2 Methodology

2.2.1 Mix design for construction blocks

A total of 4 mixed designs (including control) were formulated by replacing fly ash with BC. For each mixed design, the fly ash was replaced at 2%, 4%, and 6% of the total weight. The mix designs were designated as B-0, B-2, B-4, and B-6, with the number in the mix design indicating the biochar amendment rate. Considering B-2 as an example mix design, 98 gm of fly ash and 2 g of cement are mixed, followed by water addition until it reaches a proper consistency for workability, and mixed for 5 min in an automated mixer to reach homogeneity. Overall, the water was added in the range of 28–29.5% of the total weight of solids (the design mix table was presented in the Table S1). Variation in the water is noteworthy as biochar is likely to absorb more water resulting in a change in its consistency. All the samples made were of size $50 \times 50 \times 50 \text{ mm}^3$ and placed in the fog room under controlled temperature (21.0–25.0 °C) and humidity (> 95%) for curing. The 28 days compressive strength (ASTM C109-20b) of the cured BC-fly ash blocks were measured using an INSTRON 100 KN instrument with a minimum of three samples for each mix design.

2.2.2 Leaching assessment

The experimental procedure followed in this work is presented in Fig. 1b. Firstly, the batch leaching tests such as TCLP, SPLP, and availability tests were conducted on the raw fly ash without any pH adjustment and the resulting leachate concentrations were compared with the regulatory limits. If the concentration of contaminants of potential concerns (COPCs) is above the threshold regulatory limit, the detailed leaching assessment was conducted on the fly ash-BC composites in grounded form. For the grounded samples, the hydrated building blocks after 28 days curing were sieved below (1 mm) for the leaching studies and stored in the sealed bags as per USEPA regulations. All the concentrations were measured by using Microwave Plasma Atomic Emission Spectroscopy (MP-AES) and the brief procedure for the leaching tests involved in this study is presented below.

The Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) are standardized tests used to assess the leaching potential of contaminants from materials like fly ash. In the TCLP test (USEPA 1992a), fly ash is combined with a solution of acetic acid and sodium hydroxide at pH 2.88, maintaining a 20:1 liquid-to-solid ratio, and then shaken

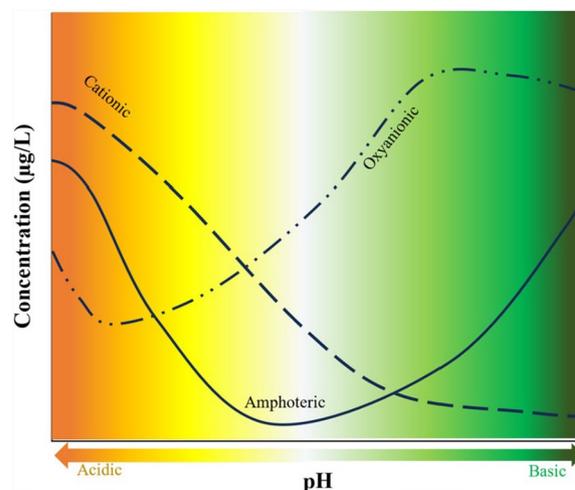


Fig. 2 Typical pH dependent leaching patterns (after Kosson et al. 1996)

for 18 h. The leachate is filtered and preserved with nitric acid for analysis. Conversely, the SPLP test (USEPA 1312 1992b) simulates acid rain conditions using a mixture of nitric and sulfuric acids at pH 4.2. Fly ash is similarly processed in this acidic solution, shaken, filtered, and preserved. Both procedures evaluate the potential environmental impact by analyzing the leachates with MP-AES.

As part of the study, the pH-dependent leaching of contaminants was evaluated using the USEPA 1313-2012 method with a parallel batch extraction procedure designed to determine the elemental composition of leachate as a function of pH. The test involves adjusting the pH of extract solutions between 2 and 13 using sulfuric acid or potassium hydroxide, with a liquid-to-solid (L/S) ratio of 10 mL extractant per gram of dry sample (g-dry). The samples were rotated at approximately 28 ± 2 rpm for a designated period. The rationale for examining varying pH levels is detailed in Table S2, emphasizing the relevance of understanding pH-dependent leaching in demolition waste, particularly as most of it is landfilled. Since landfill leachate pH changes over time, assessing these leaching behaviours is critical for modelling contaminant transport pathways.

The pH-dependent leaching of elements typically follows three trends—cationic, oxyanionic, or amphoteric—depending on the element type (Kosson et al. 2014), as illustrated in Fig. 2. To further investigate contaminant behaviour, the L/S-based leaching test followed USEPA-1316 (2012) guidelines, using five parallel extracts with L/S ratios of 10.0, 5.0, 2.0, 1.0, and 0.5 mL/g-dry, alongside a blank without solids to identify potential interferences. Samples were agitated in an end-over-end shaker

Table 2 TCLP and SPLP concentrations of various metals from the fly ash

Element	Mean TCLP concentrations (mg/L)	TCLP- Upper confidence limits (UCL 95) (mg/L)	Australia/New Zealand (AU/NZS) TCLP limits ¹ (mg/L)	Mean SPLP concentration (mg/L)	SPLP- Upper confidence limits (UCL 95) (mg/L)	USEPA DWL ² (mg/L)	New Zealand DWL ³ (mg/L)	WHO DWL ⁴ (mg/L)
As	0.05	0.05	5	BDL	BDL	0.01	0.01	0.01
Pb	0.29	0.305	5	0.01	0.01	0.015	0.01	0.01
Se	0.88	0.945	1	1	1	0.05	0.01	0.04
Cu	0.04	0.078	5	0.005	0.009	1.3	2	2
Co	0.08	0.085	NA	0.04	0.04	NA	NA	NA
Mn	BDL	BDL	NA	BDL	BDL	0.05	0.4	0.1
Cr	0.29	0.308	5	0.186	0.2	0.1	0.05	0.05
Al	0.05	0.05	40	1.67	10.84	0.2	0.1	0.1–0.2
Cd	BDL	BDL	20	BDL	BDL	0.005	0.004	0.003
Ni	BDL	BDL	10	BDL	BDL	NA	0.08	0.07
Mo	0.06	0.069	10	0.051	0.055	NA	0.07	0.01
Sr	4.13	4.22	NA	2.35	2.37	NA	NA	NA
Ba	0.635	0.774	100	0.41	0.41	2	0.7	1.3
Zn	BDL	BDL	–	BDL	–	–	–	–

DWL: Drinking water limit; BDL: Below detection limit

- <https://environment.govt.nz/publications/module-2-hazardous-waste-guidelines-landfill-waste-acceptance-criteria-and-landfill-classification/3-landfill-waste-acceptance-criteria/>
- <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations>
- <https://www.health.govt.nz/publication/drinking-water-standards-new-zealand-2005-revised-2018>
- <https://www.who.int/teams/environment-climate-change-and-health/water-sanitation-and-health/water-safety-and-quality/drinking-water-quality-guidelines>

for a specific contact period, and eluate was collected for analysis. The concentrations of eluate constituents were plotted as a function of L/S ratio, providing insights into leachate behaviour under field-relevant conditions where the tested pH and L/S ranges align with field conditions.

3 Results and discussion

3.1 Screening assessment of relevant contaminants

The leaching assessment of COPC from the fly ash was initially investigated. If the COPC concentration leached was more than regulatory limits, then a complete environmental leaching assessment of fly ash-biochar building blocks was investigated as discussed in Fig. 1b. TCLP and SPLP concentrations leached for the raw fly ash samples under natural pH conditions are summarised in Table 2. A minimum of three samples were tested and upper confidence limits (UCL) were found with the help of standard 't' values to compare with the regulatory threshold limits. For the TCLP, the leached trace elements were compared to New Zealand hazardous waste limits for disposal onto landfills. All the concentrations leached were below the regulatory limits with only a selenium (Se) concentration of 0.945 mg/L being found to be the closest to the hazardous limit of 1 mg/L.

As regulatory agencies use the SPLP test results for the risk assessment of drinking water standards (Townsend et al., 2016), an assessment is made similarly by comparing the results of the SPLP batch test and permissible values for safe drinking water issues by various regulating authorities. The SPLP concentrations were compared with drinking water limits of the World Health Organisation (WHO), USEPA, and New Zealand standards. From Table 2, it is evident that the concentrations of Se (1.04 mg/L), Al (1.84 mg/L), and Cr (1.90 mg/L) exceeded the drinking water limits under natural pH conditions. Overall, fly ash cannot be characterized as hazardous waste to dispose of into landfills. As some of the concentrations were above the drinking water limits, unscientific disposal of fly ash on the ground can contaminate the land and water bodies. So further risk assessment considering different pH and L/S ratios in terms of leaching should be explored for the major element when fly ash is reused for different applications. In consideration to higher observed values of COPC for New Zealand standards (Table 2), elements including Se, Al, Cr, and Ba were investigated for the final BC-FA building blocks through SPLP tests and batch USEPA tests considering varied values of L/S ratio. Detailed pH-based leaching was explored only for Cr and Al and the remaining COPC were found to be below detection limits.

3.2 Analytical assessment of materials and compressive strength of building blocks

The oxide composition of the fly ash with the major composition of fly ash being CaO, Al₂O₃, SiO₂, Fe₂O₃, and MgO is summarised in Table 1. The presence of SiO₂ and CaO indicates it can act both as a filler and facilitate hydration, respectively. The presence of CaO indicates that it can undergo hydration and assist in pozzolanic reactions. The oxide percentage of combined SiO₂, Al₂O₃, and Fe₂O₃ characterizes the fly ash as class C. For the BC, the compositions of major elements as per ICP-MS analysis were Si-247 mg/g, K-12 mg/g, Ca-4.6 mg/g, and Fe-0.3 mg/g. This suggests that, through ion exchange and complexation reactions among fly ash, cement, and biochar, the non-hydrated components in the dry mix (such as CaO, Al₂O₃, SiO₂, Fe₂O₃, and MgO) can undergo hydration, leading to the formation of hydrated products like Calcium silicate hydrate gels, Ca(OH)₂ crystals, and ettringite (Winters et al. 2022). Furthermore, the presence of MgO has also been implicated to long-term strength gains through the natural carbonation of CO₂ to CaCO₃ (Winters et al. 2022).

Figure 3 provides the compressive strength of the BC-fly ash building blocks tested in the current study. The BC addition increased the strength of control samples (without BC) by 10% at a 2% amendment rate. Thereafter, at a higher amendment rate, the compressive strength decreased by 6–13% for the control treatment. The increase in the strength of B-2 composites could be attributed to an improvement in the pore-filling effects as a result of improved water retention in the composite voids during hydration (Wang et al. 2021). It can also be hypothesised that the increased compressive strength due to biochar addition could be also implicated to the water present in the pores which was being released gradually allowing internal curing of concrete. Moreover, as the hydration reaction proceeds, the intra pores present in the biochar surface act as additional nucleation sites of the Calcium silicate hydrate (C–S–H) formation (Gupta et al. 2018). However, when the biochar dosage was increased by a certain amount, the more porous and thus less rigid biochar particles tended to decrease the strength of the composites as observed in an earlier study (Akhtar and Sarmah 2018a).

Another plausible reason for the decrease in the compressive strength of the composites B-4 and B-6 could be due to the available water required for complete hydration. As water was added into the matrix, most of the water at this high BC amendment rate may be consumed by the intrapore in BC due to the higher water retention capacity of BC than the fly ash. During the mixing phase, additional water was added to compensate for the decreased workability of the BC-fly ash paste. This

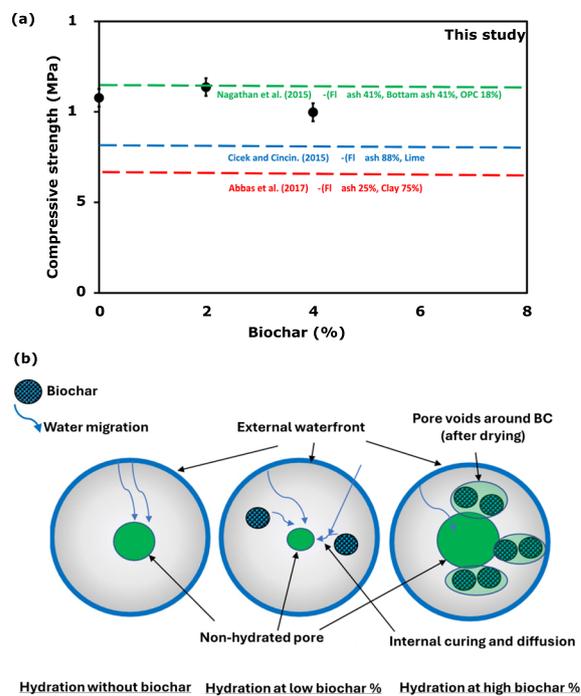


Fig. 3 28 days compressive strength of BC-fly ash building blocks (a) Schematics of internal curing provided by biochar (b)

additional water present in the BC gets released as external water film (Fig. 3b), leaving the voids in place and making the pores around the BC particle, thereby causing increased porosity of the matrix. The presence of clustered and non-uniform porosity in cementitious blocks can potentially lead to a decrease in strength (Muthukrishnan et al. 2019). Nevertheless, the compressive strength obtained from the study suggests that they can be used as fly ash bricks which necessarily requires compressive strength lower than 8 MPa (Sahu et al. 2019a, b). As per Eurocode 6 provisions, the BC-FA building blocks with 28 days compressive strength ranging from 8 to 12 MPa are suitable as masonry mortars for use in severe environmental condition (EN 1996–1-1). This implies that they would be ideal building blocks for use in non-load-bearing applications.

3.3 Leaching potential for BC-fly ash demolished blocks based on SPLP assessment

Figure 4 illustrates the concentrations of Al, Se, Ba, and Cr leached from crushed biochar-fly ash (BC-FA) building blocks based on SPLP tests. Adding biochar significantly reduced effluent concentrations, with 6% BC lowering Al, Se, Ba, and Cr levels by 72%, 48%, 58%, and 53%, respectively. The B-0 mix showed an Al concentration of 6.8 mg/L, notably lower than raw fly ash (10.84 mg/L), likely due to the greater surface area of raw fly

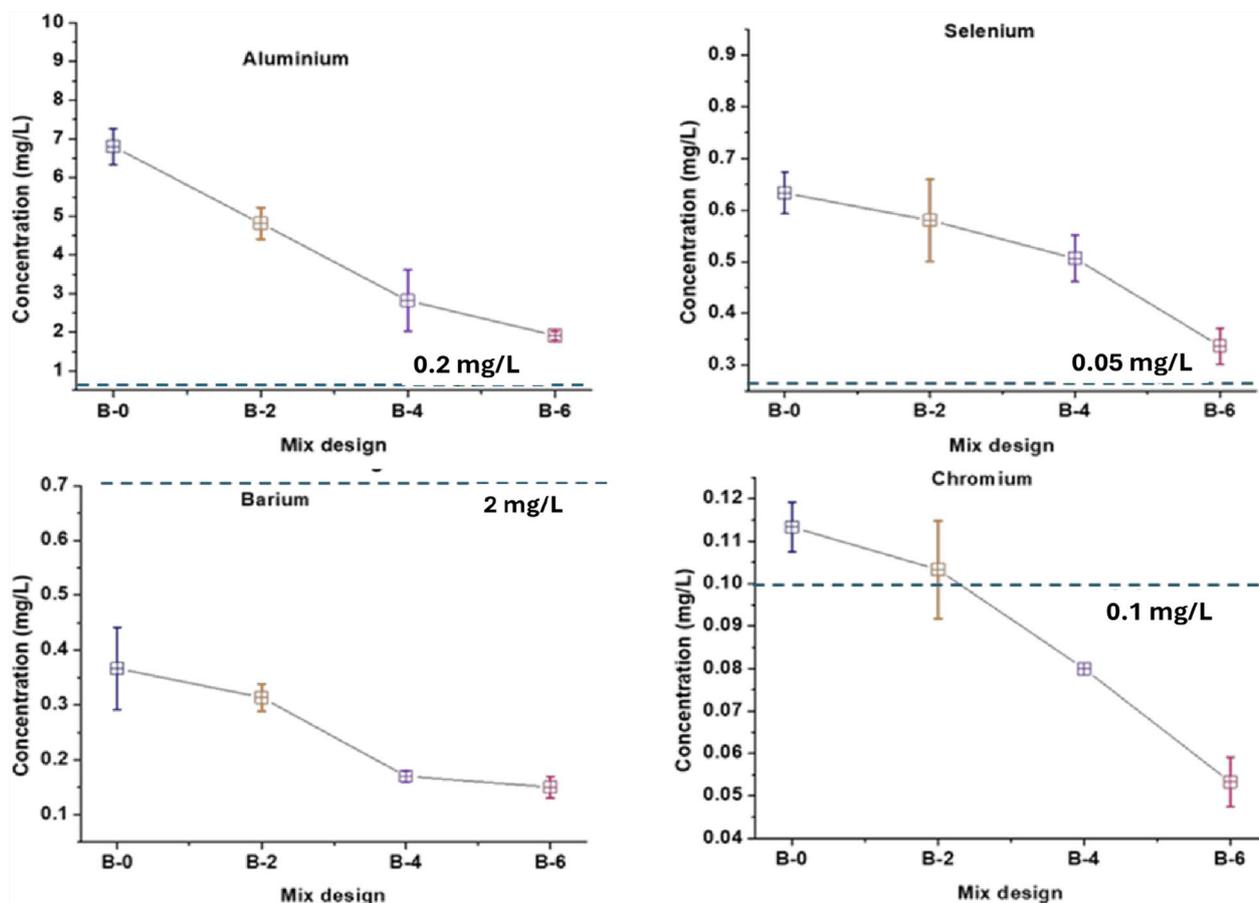


Fig. 4 SPLP concentrations of BC-fly ash building blocks

ash compared to crushed blocks (< 1 mm). However, Al and Se concentrations for all mix designs remained above USEPA, NZ Water Safety, and WHO drinking water limits. In contrast, Cr concentrations for B-4 and B-6 mixes (0.08 and 0.05 mg/L) fell below USEPA standards.

The results imply that the studied blocks as construction demolition waste could potentially cause contamination with Al, Se, and Cr, however, the risk is deemed to be significantly low with the addition of biochar in the building blocks particularly when Cr and Se are considered. Overall, the concentration of leached elements decreased with BC addition as the high cation exchange capacity of BC adsorbs some metals either through precipitation or by forming complexes with the surface functional groups. One of the potential ways to mitigate Al toxicity altogether can be the pre-treatment of fly ash by acid washing before making blocks to reduce the potential leachate (Seferinoğlu et al. 2003). The eluate can be utilized for elemental recovery operations as commonly applied for coal combustion ashes (Seferinoğlu et al. 2003).

3.4 Leaching potential for BC-fly ash demolished blocks as a function of liquid–solid ratio

Metal leaching (Al, Se, Ba, and Cr) from the building blocks as a function of L/S is presented in Fig. 5. Overall, leaching concentration decreased with the increase in the L/S ratios for all four contaminants. This is ideally expected as the contaminant diffusion is dependent on the concentration gradient. The highest concentrations were reported at L/S-0.5 for all the metals (da Silva et al. 2018). Nevertheless, BC addition in the mixes gradually reduced the metal concentrations at any considered L/S ratio. For instance, a 42% decrease in Al was observed at 6% BC amendment rate as compared to those without any BC. Similar patterns for the B-6 mixes at L/S-0.5 were observed considering Se, Br, and Cr with 41%, 72%, and 20% reduction in concentrations, respectively. As observed for SPLP tests, Al concentrations were found to be above the regulatory limits (0.1–0.2 mg/L) set for drinking water. Similar observations for Al were also reported for the demolition waste by Gupta and Kua (2018). The results have implications on the final disposal conditions of these mixes and expected leachate

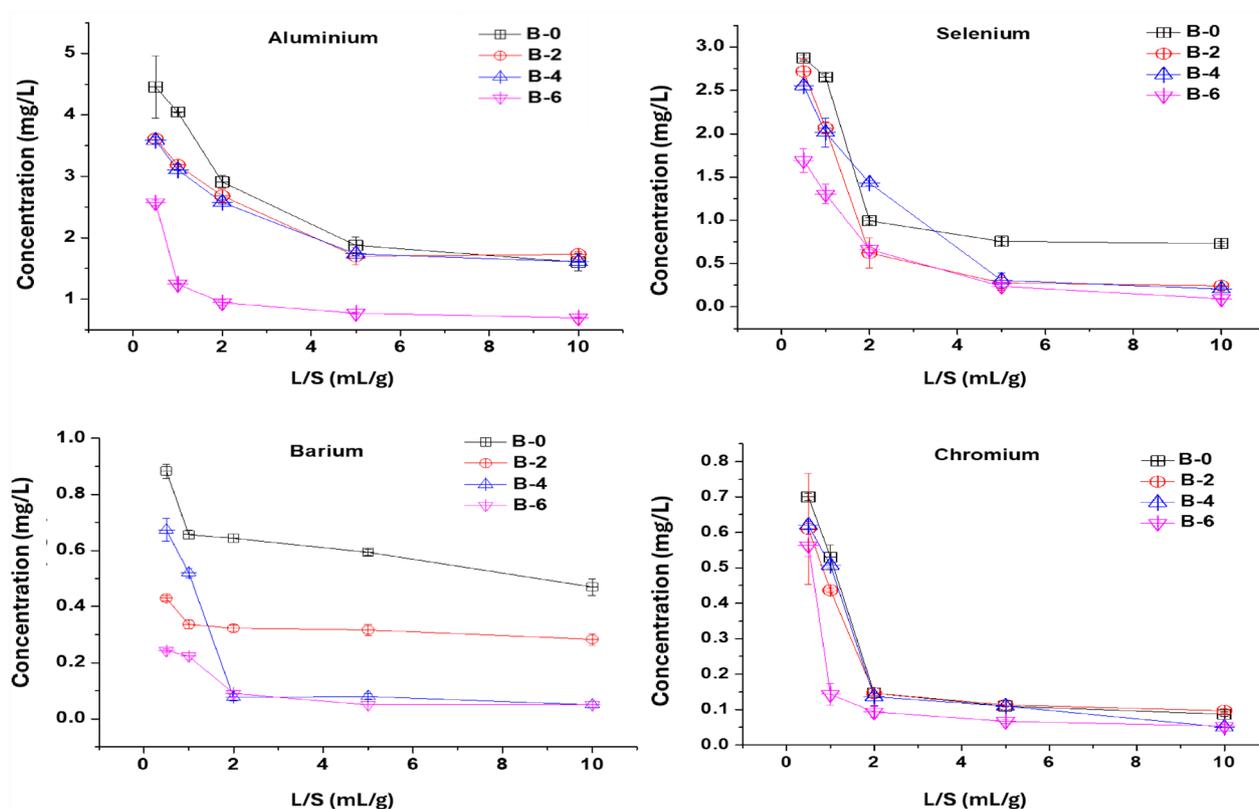


Fig. 5 Leachate concentration of selected metals from the crushed BC-fly ash building blocks as a function of L/S ratio

concentration upon barrier failure for waste containment facilities. It is noteworthy that these drinking water limits for Al are based on secondary limits (taste and odour). The observed concentration of Al does not have a direct adverse effect on human health. In case of barium, all the mixes had leachate concentrations below the regulatory limits which did not necessarily require further risk assessment. Chromium concentration for B-0 and B-2 at all L/S exceeded the drinking water limits while it remained below the limits for B-4 and B-6 at higher L/S ratios (5 and 10). Therefore, pH dependent leaching assessment was done for Cr and Al.

3.5 pH dependent leaching potential for BC-fly ash demolished blocks

Figure 6 illustrates the effluent concentrations of aluminium (Al) and chromium (Cr) across varying eluent pH levels. Both highly acidic (pH 2–3) and strongly alkaline (pH 12–13) conditions induced substantial leaching of Al and Cr. Under extreme acidity, elevated metal release likely stems from the dissolution of mineral phases hosting these metals, as observed in prior studies (Yin et al. 2018). Aluminium exhibited a distinct amphoteric “U-shaped” leaching trend, whereas Cr followed

an oxyanionic pattern. Notably, biochar (BC) addition showed negligible influence on leaching across all pH ranges, suggesting that pH exerts dominant control over contaminant binding/removal capacity, overwhelming the potential effects of BC. For amphoteric metals like Al, hydroxide dissolution critically governs solubility (Komonweeraket et al. 2015).

Al concentrations peaked at 20 and 19 mg/L under pH 2 and 3, respectively, plummeting to 4 mg/L at pH 4.2 and stabilizing until pH 5.6. Neutral conditions (pH 6.5–7.5) minimized leaching (0.7 mg/L at pH 7.5), driven by the precipitation of low-solubility amorphous $\text{Al}(\text{OH})_3$. Here, $\text{Al}(\text{OH})_2^+$ dominated and formed complexes with Ca^{2+} , facilitated by the higher reactivity of Ca^{2+} relative to Al^{3+} (Mahedi et al. 2019). Alkaline conditions (pH > 10) sharply increased solubility via $\text{Al}(\text{OH})_4^-$ formation, elevating Al^{3+} levels (Izquierdo and Querol 2012). Alarmingly, Al concentrations surpassed USEPA drinking water standards at all pH levels except near-neutral ranges. These values were in stark contrast to those reported by Lee et al. (2022) and Zhang et al. (2016) for MSW landfill leachate, and fly ash leachate respectively as shown in Fig. 6.

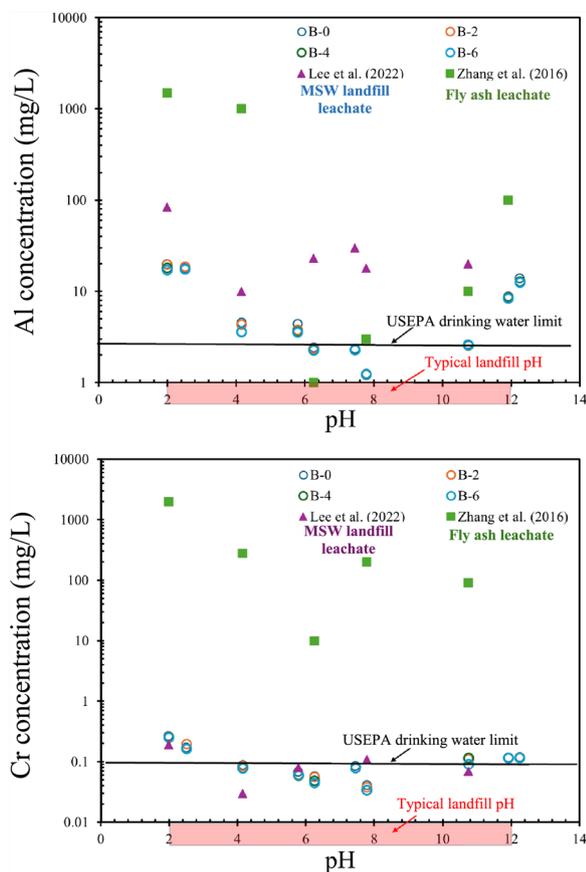


Fig. 6 pH dependent Al and Cr concentrations of the crushed BC fly ash building blocks

Cr leaching, governed by $\text{Cr}(\text{OH})_3$ and Cr_2O_3 solubility (Gitari et al. 2009), mirrored Al in its pH dependency. Minimal Cr release occurred near neutral pH (4–9), likely due to Cr^{3+} reduction by Al^{3+} (Quina et al. 2009), with concentrations within USEPA limits. However, acidic ($\text{pH} < 3$) and alkaline conditions triggered sharp increases (0.25–1.7 mg/L), linked to the dissolution of chromium oxides/hydroxides (Komonweeraket et al. 2015). Alkaline-driven Cr mobilization aligns with the dominance of carcinogenic CrO_4^{2-} (Shoji et al. 2002; Zhao et al. 2020), while low-pH leaching arises from protonation-induced desorption of oxyanions (Dijkstra et al. 2006) and Cr release from fly ash aluminosilicates (Neupane and Donahoe 2013). These findings corroborate Dubikova et al. (2006), who observed similar pH-dependent Cr leaching plateaus ($\text{pH} 8\text{--}12$). A comparison with Cr data from literature (Zhang et al. 2016) suggested that Cr concentrations in fly ash leachate were significantly higher than those reported in our study and as well as those reported by Lee et al. (2022) in municipal soil waste landfill leachate.

Overall, Aluminium's amphoteric leaching arises from the dissolution of $\text{Al}(\text{OH})_3$ at $\text{pH} < 4$ (Al^{3+} release) and $\text{pH} > 10$ ($\text{Al}(\text{OH})_4^-$ formation). Chromium's oxyanionic behavior reflects Cr(VI) dominance at alkaline pH as CrO_4^{2-} , while Cr(III) precipitates as $\text{Cr}(\text{OH})_3$ at neutral pH. BC's limited pH buffering explains its minimal influence on Cr/Al leaching trends.

This leaching framework expands the range of tools available for decision-making, offering valuable insights into the behavior of various elements through leaching test procedures. These tests facilitate a more comprehensive risk assessment by explaining why certain elements behave in specific ways. The combination of regulatory tests, such as TCLP and SPLP, with more detailed evaluations (e.g., pH and liquid-to-solid ratio tests) creates a structured approach that assists landfill operators and regulatory authorities in making site-specific decisions, such as determining whether waste should be repurposed beneficially or disposed of, particularly in cases involving secondary wastes like construction and demolition debris. The flexibility to the framework allows decision-makers to tailor its application based on the level of information required. For instance, if only a single contaminant concentration threshold is needed for a straightforward Yes/No dumping decision or hazardous waste classification, basic regulatory tests within the framework suffice. By incorporating key influencing factors such as pH and leaching duration, this framework enhances the accuracy of assessments, producing results that closely reflect real-world field conditions. Additionally, future work should explore (1) the column studies to simulate field conditions, (2) increased biochar addition and functionalization for enhanced metal binding, (3) lifecycle assessment to quantify net CO_2 savings, and (4) biological leaching (e.g., microbial weathering).

4 Conclusion

Through this study, we provided an assessment of BC-fly ash building blocks for their mechanical strength and their metal leaching potential in a crushed state mimicking their end-life conditions. The metal leaching assessment involving TCLP, SPLP, and EPA regulatory batch tests provided insights into any potential leaching scenarios related to its disposal and the major conclusions were drawn as below:

1. As per Eurocode 6 provisions, the BC-FA building blocks with 28 days compressive strength ranging from 8 to 12 MPa is suitable as masonry mortars for use in severe environmental condition. The highest compressive strength among all mixes was observed at a lower BC amendment rate at 2% by weight, wherein BC acted as a suitable pore filling agent and

likely provided additional localized curing during the hardening phase.

- The TCLP concentrations for all COPC in the FA were found to be below the hazardous waste disposal criteria on the landfill, indicating the safe discharge on the engineering landfills. The SPLP concentrations of some of the elements Al, Cr and Se exceeded the drinking water standards indicating potential risk assessment needed for the blocks in the reuse scenario.
- The SPLP concentrations decreased for the biochar-added mix designs. The Al, Se, Ba, and Cr concentrations were reduced by 72%, 48%, 58%, and 53% on adding 6% of the biochar, respectively. Aluminium and Selenium SPLP concentrations were found to be above the drinking water limits for all the mix designs, while Cr concentrations for B-4 and B-6 were below USEPA threshold limits.
- The leachate concentrations of Al, Se, Ba, and Cr decreased when the L/S ratio was increased from 0.5 to 10. Nevertheless, the gradual addition of BC decreases the major contaminants significantly even at low L/S. For Al, the concentrations were above the drinking water limits at all mix designs, with Cr concentrations for B-4 and B-6 at higher L/S ratios (5 and 10) below the drinking water limits.
- The concentrations of Al and Cr as a function of pH show the typical amphoteric and Oxyanionic pattern, respectively. The highest concentrations leached at extremely acidic conditions with minimal release in the neutral conditions, typically lower than DWL.

Overall, the holistic leaching study focused on selected elements of environmental concerns, providing valuable insights into the leaching behavior at final disposal conditions. It is envisaged that the findings obtained through this investigation could be used as essential baseline information for geochemical modelling and the identification of leaching control mechanisms of BC-FA demolition waste disposal systems.

Supplementary Information

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Additional file 1.

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Author contributions

The first author (Sai Praneeth) drafted the manuscript based on concepts jointly discussed with the third author (Ajit K. Sarmah). The second author (Sanandam Bordoloi) plotted several figures and overall visualised the manuscript and commented on the original and revised manuscript. The first author (Sai Praneeth) also helped to revise the entire manuscript a few times based on technical advice. The corresponding author (Ajit K. Sarmah) reviewed, supervised the work, validated, and reviewed the manuscript. All authors read and approved the final manuscript.

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Data availability

The datasets used or analysed during the current study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

Ajit K. Sarmah is an EBM of the journal *Biochar*, but he was not involved in the peer-review or handling of the manuscript. The authors have no other competing interests to disclose.

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